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Herz chemistry and its applications in small-molecule functional materials science: achievements, challenges, and prospects

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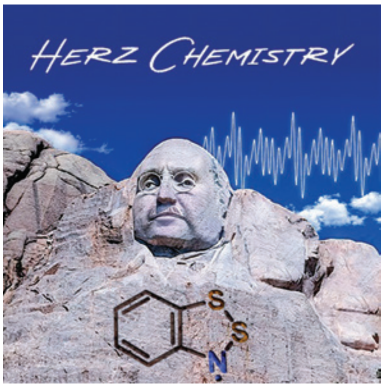
This review discusses the achievements of Herz chemistry over its first century, together with challenges and prospects. The discussion focuses on the synthesis, structure, and reactivity of various closed- and open-shell chalcogen-nitrogen π-heterocyclic species. The latter are derivatives of the (het)areno-fused 1,2,3-dichalcogenazole ring system with S, Se, and less often Te, chalcogens in various spin and charge states encompassing cations, radicals, bipolar ions, and quinoid antiaromatics/diradicaloids. They are important for fundamental chemistry and materials science, specifically for the design and synthesis of metal-free conductive, magnetic, and optoelectronic materials. The potential for further extension of Herz chemistry to other non-transition elements is also considered. A comparative analysis of Herz species and their 1,3,2-isomers (Wolmershäuser species) is provided.
The bibliography includes 344 references.

Keywords: chalcogens (sulfur, selenium, tellurium), 1,2,3- and 1,3,2-dichalcogenazoliums/yls, open-shell species, bipolar ions, quinoids, antiaromatics, synthesis, structure, reactivity, metal-free conductors and magnets.



Contents

1. Introduction

The chemistry and applications of 1,2,3-benzodithiazoles were initiated a century ago by Richard Herz (1867–1936)[1] with the cyclization of $ArNH_2$ into 1,2,3-benzodithiazoliums (Herz cations, HCs), *e.g.*, **1** (Scheme 1), by the action of S_2Cl_2 and their isolation in the form of chloride salts (Herz salts, HSs). The cyclization revealed the general nature and wide industrial applicability for the production of various synthetic dyes, and was named the Herz reaction.[2–13] Its limited extension to $HetNH_2$ is the hetero-Herz reaction.[13–18] Both reactions belong to various chemical transformations involving organic amines and sulfur halides.[12,19–23] Other milestones in the field include the EPR detection of persistent 1,2,3-benzodithiazolyls (Herz radicals, HRs), *e.g.*, **2** (see Scheme 1) as the key intermediates of the Herz reaction by Roland Maier (1927–2013)[24] *et al.*;[18,25–27] extension to Se derivatives by Lev S. Éfros *et al.*;[28–30] isolation of HRs in the form of thermally-stable solids with conductive and/or magnetic properties by Richard T. Oakley *et al.*;[31–43] generation of otherwise inaccessible HRs, *e.g.*, polyfluorinated, by thermolysis or UV photolysis of polysulfur-nitrogen rings; and direct preparation of analytically pure HSs by reaction of 1,2,3,4-benzodithiadiazines with SCl_2.[38,44,45] Important bioactivity of Herz species relates mostly to monocyclics.[46,47]

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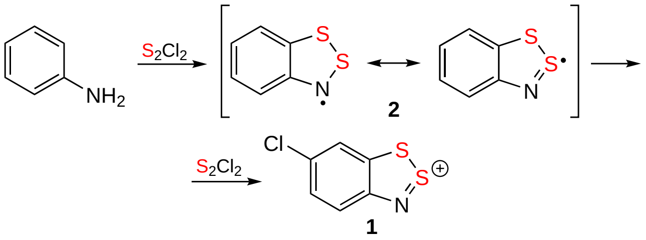
Scheme 1



Formally, HCs and HRs are π-heterocyclic derivatives of NS^{+} and $NS^{\bullet}$, respectively, which have been observed in interstellar space, and $NS^{\bullet}$ has also been found in the coma of comet Heil–Bopp;[48–55] EN^{+} and $EN^{\bullet}$ (E = Se, Te) have been studied to a lesser extent.[50,51,56] Stable acyclic derivatives of $NS^{\bullet}$ are thioaminyls.[57,58]

Herz chemistry is highly relevant and rapidly developing as an integral part of *polysulfur-nitrogen* chemistry,[59,60] which is currently evolving into *polychalcogen-nitrogen* chemistry,[61–64] which is itself part of *main group* chemistry (*i.e.*, chemistry of the elements from the groups 1, 2, 13–18). The family of Herz species includes variously substituted/annulated 1,2,3-benzodichalcogenazoles and encompasses cations, radicals, radical ions, and neutral molecules (Figure 1). The latter can be classified as antiaromatic quinoids (Herz quinoids, HQ), bipolar ions, and/or singlet diradicals/diradicaloids, and they have attracted significant interest in current main group chemistry.[2,13,43,65–73]

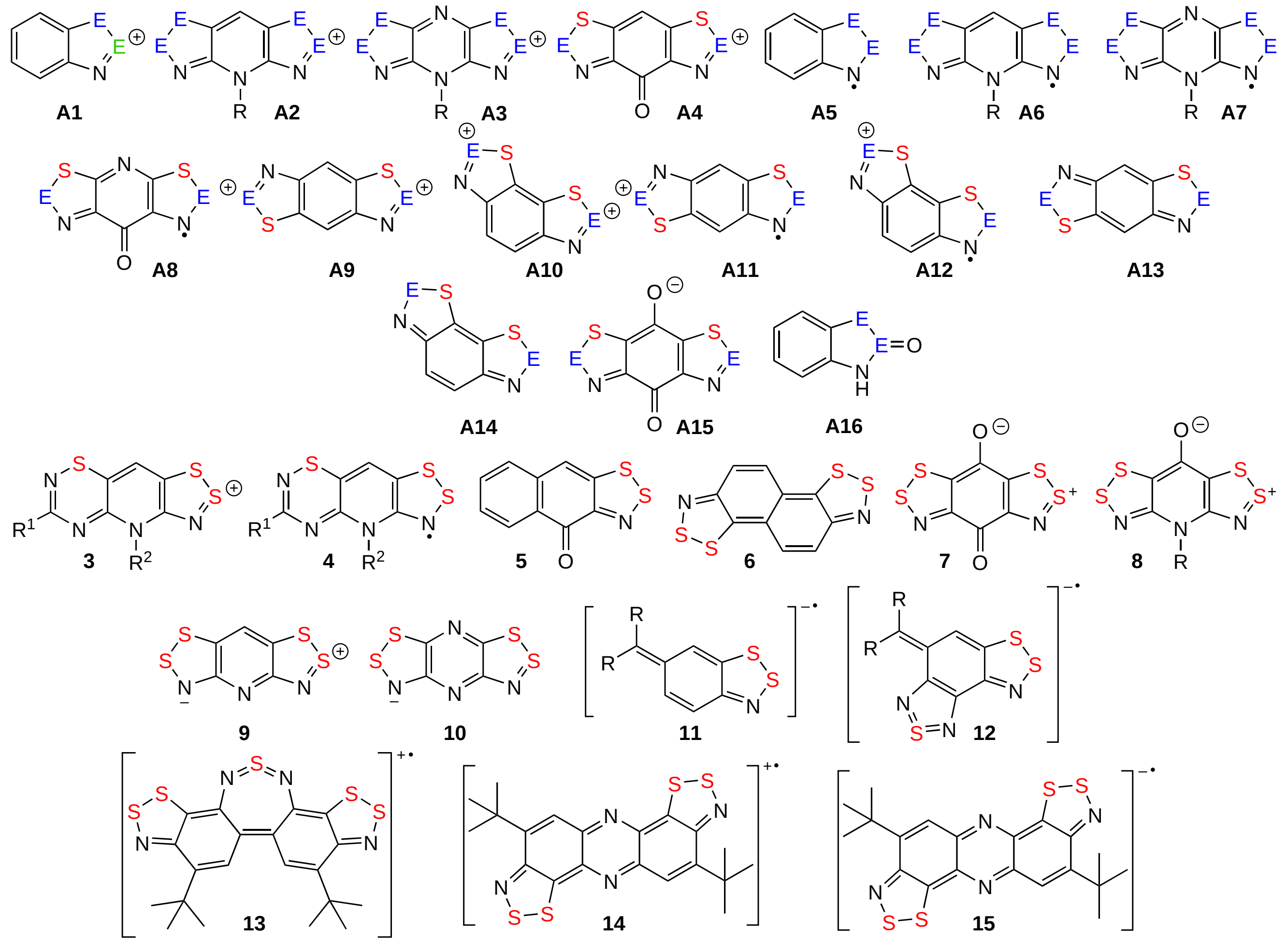


Figure 1. Representative **A1-A16** archetypical (E = S, Se; E = S, Se, Te) and specified **3**–**15** Herz scaffolds. For simplicity, from now on, π-delocalized HRs are shown as N-centred to avoid resonance superpositions.

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For species with two radical centres, it is reasonable to distinguish between diradicals and disradicals; the former reveal significant ($J \neq 0$) and the latter insignificant exchange interaction ($J \sim 0$) between the paramagnetic centers.[72] Of particular importance are real and/or putative high-spin ($S \geqslant 1$) Herz di- and polyradicals[74,75] — by themselves and as parts of a large family of persistent and stable metal-free high-spin species.[73,76] Overall, Herz species are intriguing due to their multifaceted functionalities in chemistry. Particularly, they exhibit ring-modification, -contraction, and -opening reactions, and are involved in the synthesis of various compounds that are otherwise difficult to access.[77–80] Additionally, they are important for materials science as conductive, magnetic, and optoelectronic materials.[74,75,81–85] Acyclic aminodisulfide analogues of Herz species are also of great current interest in chemistry, materials science, and life sciences.[86]

Herz chemistry and its applications have been discussed in numerous review articles and book chapters, primarily focusing on S derivatives, monoradicals, and functional materials.[2,3,5,6,43,47,69–71,81–84,87–89] In addition to updating these topics, this review expands to include heavier-chalcogen species, high-spin radicals, radical ions, and neutral quinoids (singlet diradicals/bipolar ions). The overall goal of this review is to examine Herz chemistry and its applications within the broader framework of *main group* chemistry. Consequently, this review is more conceptual than descriptive. For this reason, and for clarity, in Chapter 2 (Synthesis and reactivity), reaction byproducts and substituents in Herz species, including annulated derivatives, are unspecified/omitted where not significant; *i.e.*, the main emphasis is made on the transformations of scaffolds. Similarly, HS anions are typically $[Cl]^-$ unless otherwise indicated; π-delocalized HRs are depicted as N-centred (*cf.* Figure 1) to avoid resonance superpositions. However, the substituents and anions are specified in Chapters 3 (Molecular and electronic structure), 4 (Crystal structure), and 5 (Materials science). Units/dimensionalities of physical quantities and abbreviations are specified in Abbreviations and units Section.

The synthesis and reactivity of Herz species are considered together because of the interconvertiblity of the compounds; less studied are 3*H*-1,2,3-benzodithiazole 2-oxides (Herz bases, HBs), which contain the S(IV) asymmetric atomic centers and can introduce chirality into reaction products. In terms of reactivity, the main focus is on heterocyclic transformations; the carbocyclic reactivity of Herz species is typically associated with nucleophilic or radical substitution. HCs and HRs are systematically compared for the first time with isomeric 1,3,2-benzodithiazoliums and -dithiazolyls (Wolmershäuser cations and radicals; WCs and WRs, respectively).

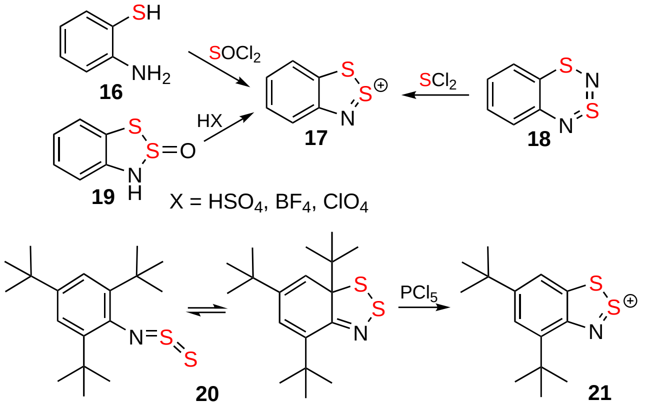
Monocyclic Herz species are not considered in this review, with the exception of their involvement in the synthesis of HQs. The best known of these is AC,[90] which has a different chemistry to HCs.[47,74,91–94] Monocyclic radicals, unlike HRs, demonstrate a tendency to C-centred recombination and are stable only when the corresponding reaction centres are sterically hindered;[87,95–98] bicyclic radical cation representing tetrathiadiazafulvalene scaffold[98] is stable enough to be isolated in the form of salts.[94]

2. Synthesis and reactivity

2.1. Cations and radical cations

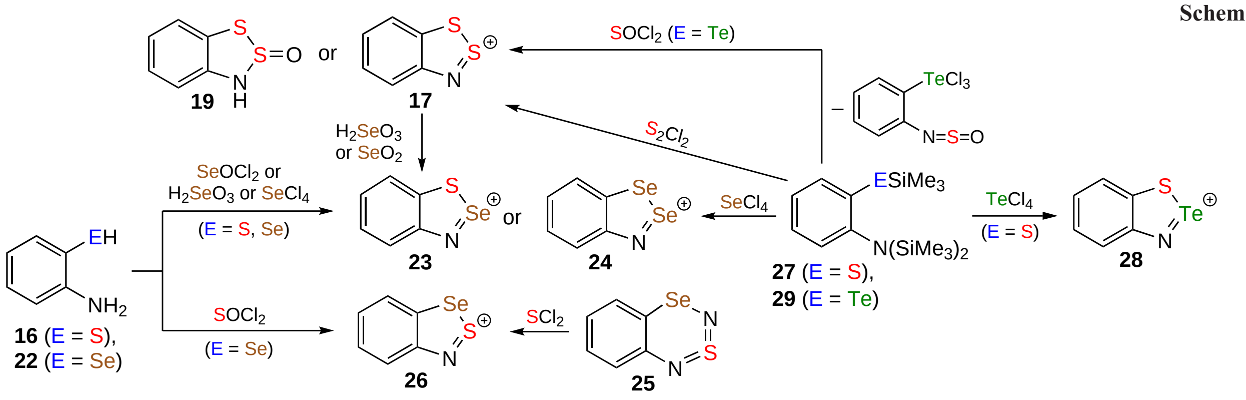
In addition to the Herz and hetero-Herz reactions,[2–9,12–18,89,99] four other preparative approaches include the reaction of 2-aminothiophenols or their N–R derivatives with S_2Cl_2 or $SOCl_2$;[3,4,13,33,38,40,41,89,100] the reaction of 1,3,2,4-benzodithiadiazines with SCl_2;[13,44,101–103] the treatment of HBs with strong acids;[7,13,89,104–106] and the reaction of 7a*H*-1,2,3-benzodithiazoles with PCl_5 (Refs 89, 107, 108) (Scheme 2). These approaches utilize ring-closure, ring-contraction, and ring-modification reactions (Schemes 1 and 2); and the approach based on aminothiols can be considered as retrosynthetic one. The Herz reaction involves chlorination of the carbocycle at position 4 by substitution of an H atom (see Scheme 1) or an electron-acceptor group but not an electron-donor group. Non-S_2Cl_2 approaches (Scheme 2) typically avoid chlorination and the loss of the initial substituents.

Scheme 2



Preparative approaches to Se containing HCs also employ the same three reactions, with ring-modification occurring through chalcogen exchange (Scheme 3).[28,29,33,38,40,43,70,103,109,110] The only reported Te containing HC has been synthesized by a ring-closure reaction (see Scheme 3),[40] while other attempted

Scheme 3



approaches yielded Te-free HCs;[100] this underscores the unique behavior of Te among the chalcogens.[111]

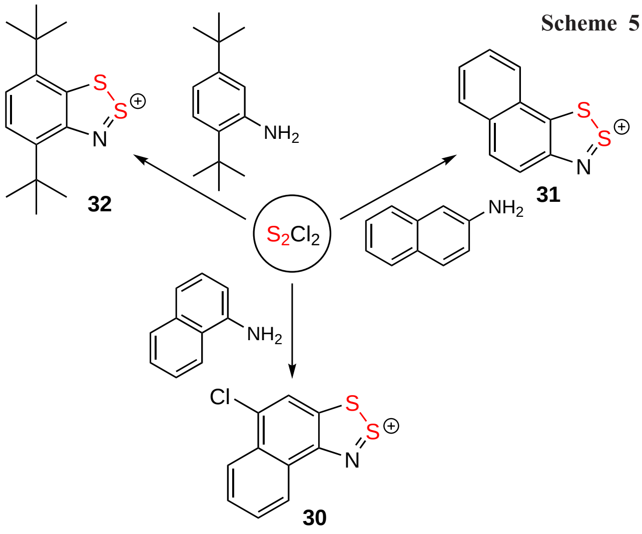
In HSs obtained by the Herz/hetero-Herz reaction, the anion is $[Cl]^-$, and they are poorly soluble in nonpolar organic solvents except Bu^t derivatives.[100,103,107] The poor solubility is likely caused by chalcogen bonding (ChB)[112,113] between HCs and $[Cl]^-$,[114] a phenomenon known for halide salts of WCs.[115,116] Replacing $[Cl]^-$ with low-coordinating anions, such as $[MCl_4]^-$ (M = Al, Ga, Fe), $[SbCl_6]^-$, $[CF_3SO_3]^-$, $[ClO_4]^-$, *etc*., improves solubility and enhances the general utility of HSs in various preparations and applications.[7,32,38,39,41,71,114,117]

2.1.1. Herz and hetero-Herz reactions

The Herz reaction is primarily limited to S chemistry and is used for single and double ring-closures. Attempts to extend the reaction to heavier chalcogens using E_nCl_2 (E = Se, Te; $n = 1, 2$)[118–124] have not been reported. The reaction has a wide scope, encompassing numerous carbocycle- and N-functionalized (–NH–OH, –NH–NH$_2$,–N=O, –N=S=O, =N–OH) substrates, including nonbenzoid ones. The substitution/annulation patterns of HCs exhibit considerable diversity, which is significant for both fundamental chemistry and applications. Reaction conditions are crucial, including solvent dependence.[2–6,9,10,13,20,89,100,103,114,117,125–128] In the presence of organic bases, *e.g.*, DABCO or Et_3N, the reaction route is changed to Ar–N=S=N–Ar and/or A–N=S=S instead of HCs.[129,130] $ArNH_2$ with an *ortho* Me groups give 2,1-benzoisothiazoles[131] (*cf.* similar cyclization of *ortho*-methylated $[ArNSN]^-$ anions);[132] and those with *ortho* NH_2 groups, 2,1,3-benzothiadiazoles.[133,134]

In the Herz reaction, the reagent S_2Cl_2, typically used in excess with respect to $ArNH_2$, has both oxidizing and chlorinating properties.[11,19,21,22,135,136] The oxidizing ability is essential for the transformation of the intermediate HRs into the final HCs (Scheme 4).[23,25] Elemental chlorine generated during the reaction also participates in both oxidation and carbocycle chlorination.[9] The latter is a hallmark of the Herz reaction. Generally, chlorination occurs at the *para*-position to the N-function if the position is unsubstituted (see Scheme 4) or carries an electron-acceptor group. An electron-donor group at this position remains intact, and chlorination occurs at another position, such as the *ortho* position in the case of Ar = 4-AlkOC$_6$H$_4$.[137] Bulky substituents or annulation prevent chlorination (*cf.* HCs **30**–**32**; Scheme 5).[11,103] However, full understanding is complicated by byproducts including chlorinated/nonchlorinated and cyclic/acyclic.[23,136,137] Particularly, in the reaction $ArNH_2 + S_2Cl_2$ (Ar = 4-MeOC$_6$H$_4$) at 70°C the major non-chlorinated HS was formed along with minor *ortho* chlorinated one; whereas at 50°C *ortho* chlorinated $ArNH_2$ was observed as the major product, together with minor target HS.[137]

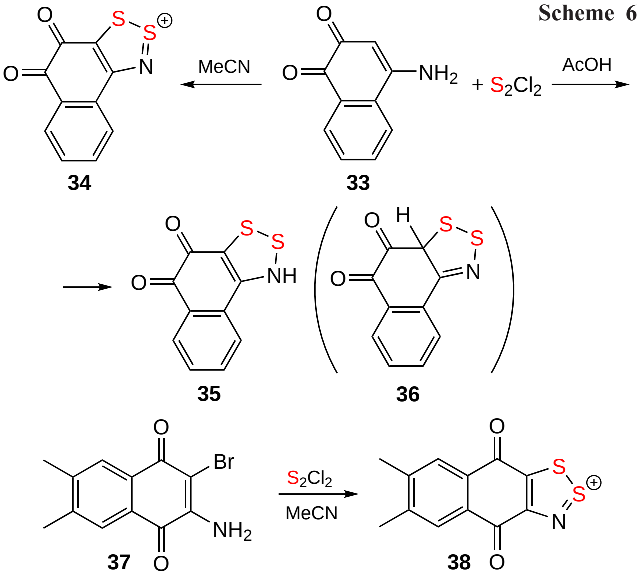
Scheme 5



32 **31** **30**

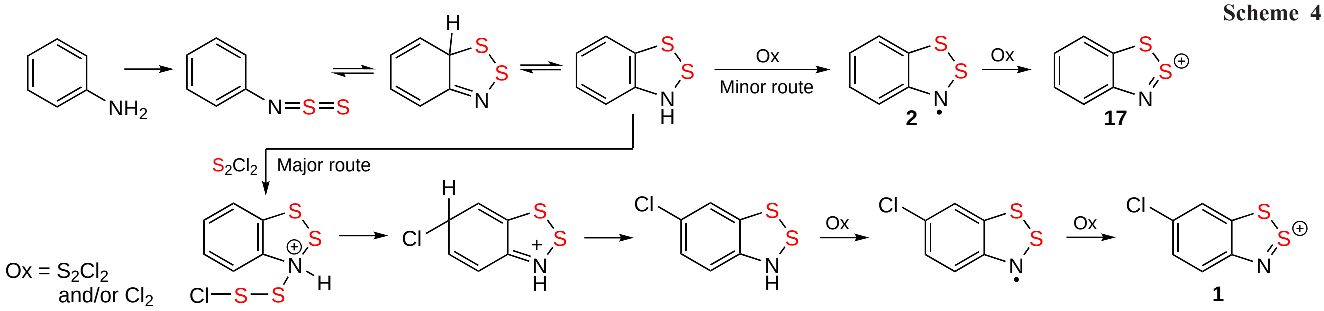
The ring-closure in the Herz reaction is regioselective, *e.g.* cyclization of 2-acetamidonaphthalene proceeds at position 1.[99] The reaction of naphthalene derivative **33** with S_2Cl_2 leading to HC **34** in MeCN[114] and 3*H*-1,2,3-dithiazole **35** in AcOH (alternative product **36** is not observed) gives an example of solvent dependence (Scheme 6).[138] The ring-closure reaction can also involve leaving groups other than H atoms. Particularly, the transformation **37** → **38** and synthesis of **39** demonstrate the utilization of a Br atom and carboxyl group, respectively (Scheme 6 and Scheme 7).[139,140] For benzo-fused heterocycles, a bifurcation between Herz and hetero-Herz pathways occurs

Scheme 6



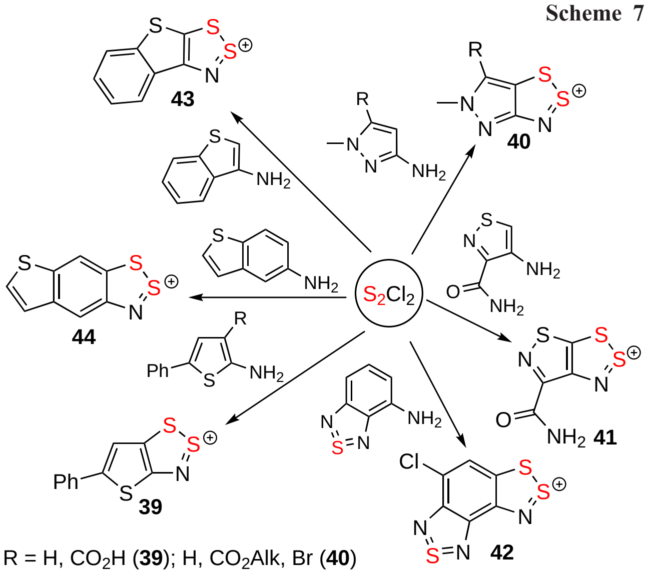
34 **33** **35** **36** **37** **38**

Scheme 4



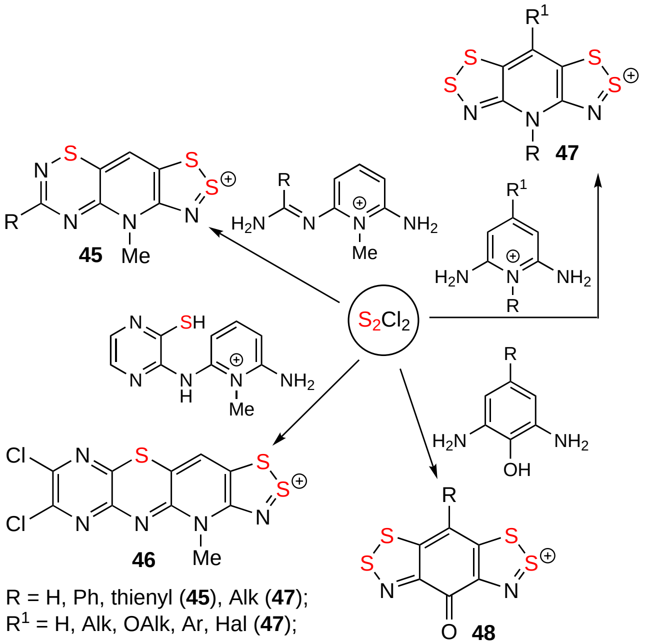
2 **17** **1**

Scheme 7



R = H, CO_2H (**39**); H, CO_2Alk, Br (**40**)

Scheme 8



R = H, Ph, thienyl (**45**), Alk (**47**);
R^1 = H, Alk, OAlk, Ar, Hal (**47**);
Me, Ph, NO_2 (**48**)

depending on the position of the NH_2 group.[13–15,18,130] Overall, the approach encompasses a wide range of heterocyclic substrates, including thiophenes, pyrazoles, isothiazoles (but not isoxazoles),[17,18] and benzothiadiazoles[125,141] (*cf.* HCs **39**–**44**) (see Scheme 6 and Scheme 7).

The hetero-Herz reaction, accompanied by additional cyclization processes, and the double (hetero)-Herz reaction, lead to the formation of polycyclic HCs **45**–**48** (Scheme 8)[16,35,127,142–154] and RCs **49** and **50**, together with chlorinated derivatives **51** and **52** of the latter (Scheme 9). For isolation and identification, **49** and **50** were chemically reduced into corresponding closed-shell HQs **6** and **53**. Subsequent chemical and electrochemical oxidation of these HQs gave the chloride salt of dication **54**, and/or mixed-valence HSs **55**–**57** (see Scheme 9).[31,32,155–157]

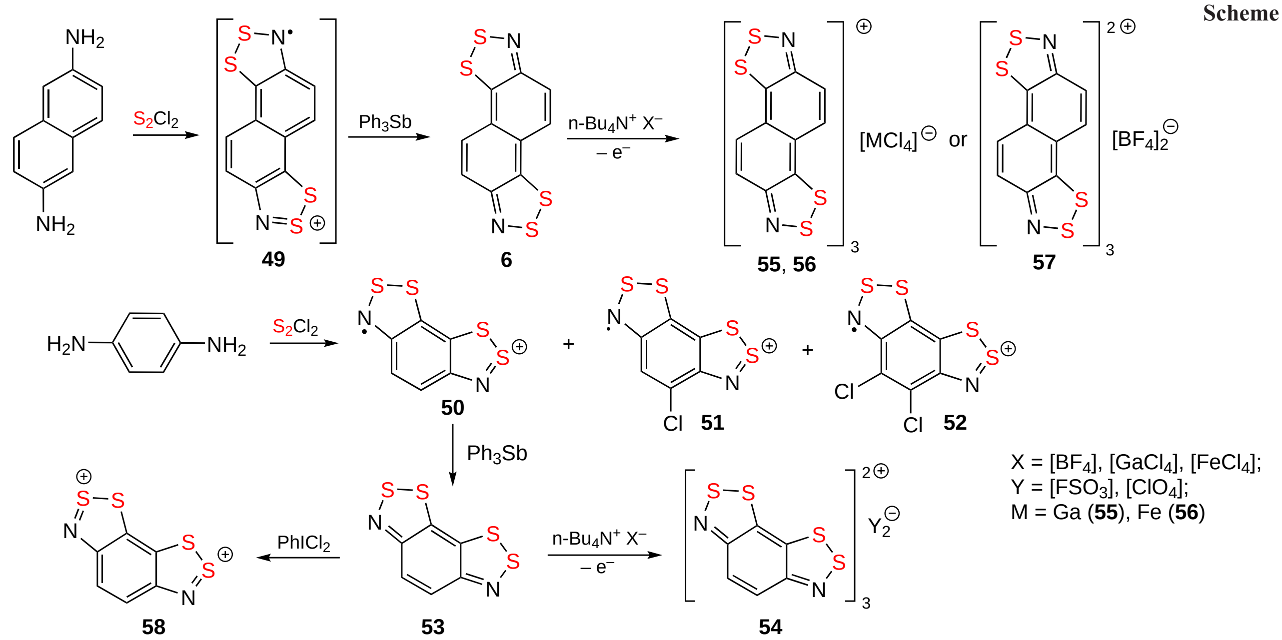
The Herz and hetero-Herz reactions appear to involve multiple stages, and the overall situation regarding regioselectivity of ring-closure, carbocyclic substitution, and solvent dependence is rather intricate, necessitating further research, mainly through quantum chemical modeling. The inherent chlorination is not necessarily a drawback, as halogenated Herz species hold a particular interest (see below).

2.1.2. Other ring-closures

Alternative ring-closure methods to the Herz/hetero-Herz reaction encompass S, Se, and Te containing substrates and are facilitated by $SOCl_2$, S_nCl_2 (n = 1, 2) and PCl_5 reagents. The reaction of 2-aminothiols with $SOCl_2$ yields nonchlorinated HCs, whereas S_2Cl_2 or S_2Cl_2/Cl_2 afford chlorinated products. The alternatives include $-N{=}PR_3$ derivatives instead of $-NH_2$ ones (Scheme 2 and Scheme 10; *cf.* Scheme 9).[2,13,32,39,40,117,158–162]

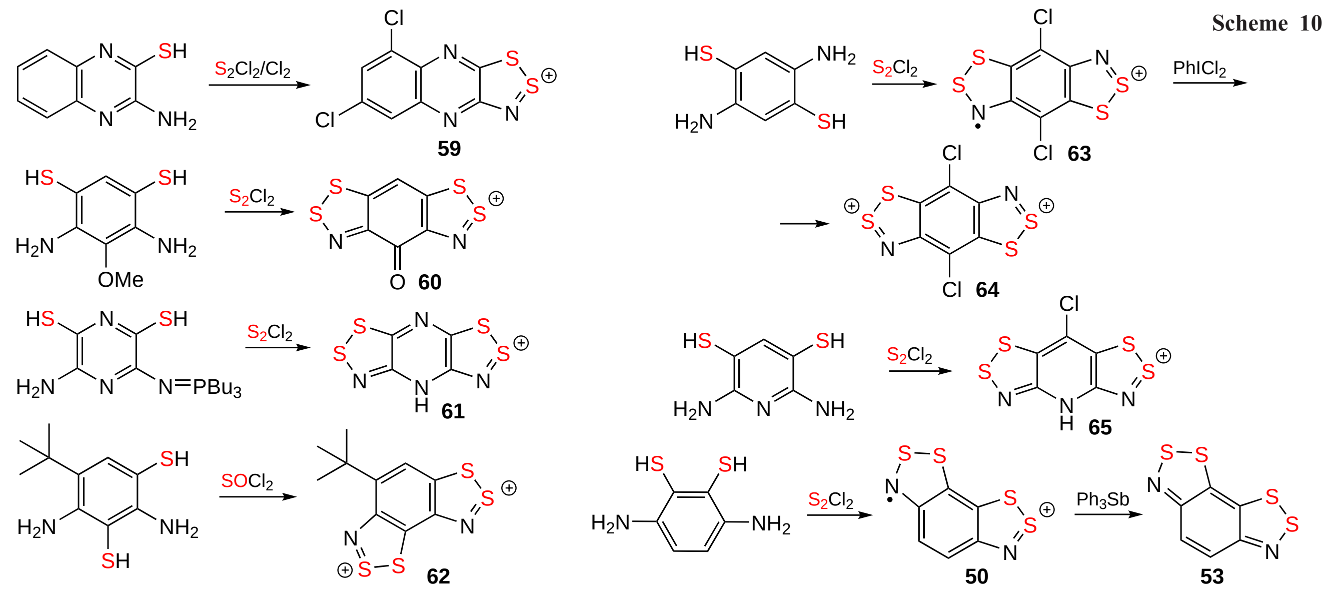
The reaction of compound **20** (existing as an equilibrium between dithiazole and N-thiosulfinyl,[138,163] a peculiarity of the N=S=S but not of the N=S=O group[130]) with PCl_5, which closes

Scheme 9



X = $[BF_4]$, $[GaCl_4]$, $[FeCl_4]$;
Y = $[FSO_3]$, $[ClO_4]$;
M = Ga (**55**), Fe (**56**)

Scheme 10



the ring of the N-thiosulfinyl and oxidatively modifies the dithiazole, provides HC **21** (see Scheme 2). Extending this singular result to other Ar–N=S=S[2,23,107,108,164] (putative intermediates of the Herz reaction, Scheme 4) remains challenging.

Reactions of 2-aminochalcogenols with $EOCl_2$ (E = S, Se), $SeCl_4$ or H_2SeO_3, and 2-aminothiol with $TeCl_4$, produce Se HCs[33,38,40,70] and Te HC,[40] respectively; whereas attempts with 2-aminotellurol derivative yielded only Te-free HCs with Te containing anions $[TeCl_6]^{2-}$, $[Te_3Cl_{14}]^{2-}$, or $[Te_4Cl_{18}]^{2-}$ (Ref. 100) (see Scheme 3).

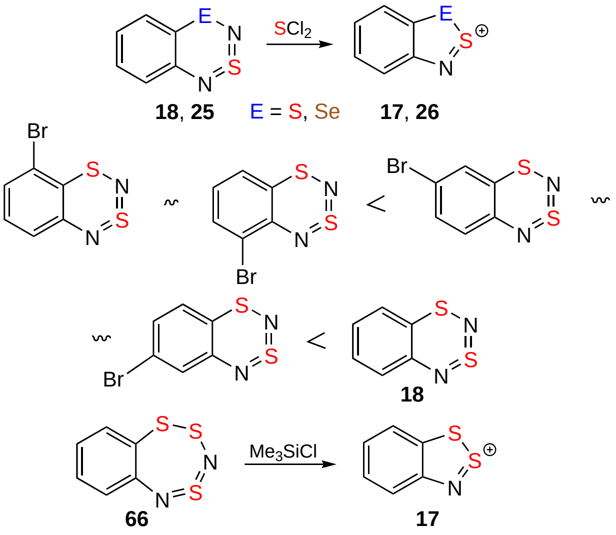
2.1.3. Ring-modifications

Ring-modification approaches encompass dehydration of S containing HBs under the catalytic action of strong protic acids, yielding analytically pure HSs, *e.g.*, that of **17**, and chalcogen-exchange in HBs, directly or through HCs, under the influence of H_2SeO_3 or SeO_2, producing Se HCs, *e.g.*, **23** (Refs 6, 29, 70, 104, 109, 146) (see Scheme 3).

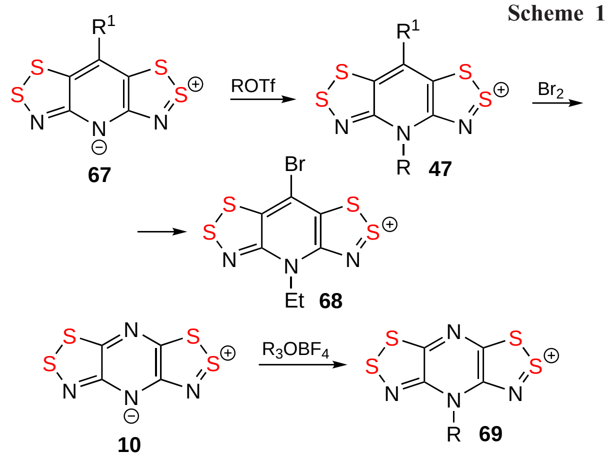
2.1.4. Ring-contractions

Oxidative hetero-ring contractions of benzo-fused dithia-/selenathiadiazines **18**/**25** with SCl_2 provide pure HSs without carbocycle chlorination (except for the 6-Me derivative of **18**). The reaction rate for **18** and its derivatives significantly depends on the nature and positions of the substituents in the carbocycle. Halogens Cl, Br, and I slow down the reaction, especially if they are adjacent to the heterocycle (for relative reaction rates of isomeric monobromo derivatives of **18**, see Scheme 11).[44,101–103] Ring contraction of **18** and its derivatives into HCs with S electrophiles C_6F_5SCl and $[NS_2]^+$ yields numerous byproducts.[82] Trithiadiazepine **66** is converted to HC **17** under the influence of Me_3SiCl (see Scheme 11); similar transformation of its 1,3,5,2,4-isomer into the corresponding WC occurs notably faster.[165–167]

Scheme 11



Scheme 12

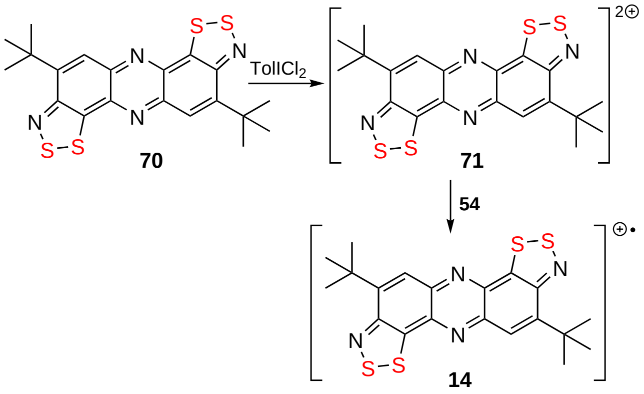


67: R^1 = H (*cf.* **9**), Cl; **47**: R^1 = H, Cl; R = Me, Et, CH_2CF_3, Pr; **69**: R = Me, Et

2.1.5. Miscellaneous

Alkylation of bipolar ions **10** and **67** with R_3OBF_4 or ROTf, respectively, generates HCs,[147,149] which can then be brominated (compounds **47**, **68**, **69**; Scheme 12).[146] Chemical oxidation of HQ **70** yields dication **71**, which comproportionates with the starting HQ to produce RC **14** (Scheme 13).[117]

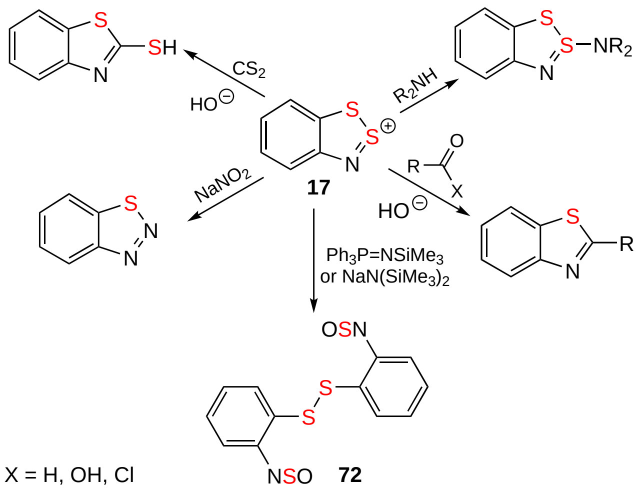
Scheme 13



2.1.6. Reactivity

HCs exhibit thermal stability. The most important chemical properties of HCs are the reduction to HRs (below) and hydrolysis to HBs. Under mild hydrolytic conditions, S-HCs convert into S-HBs; whereas Se-HCs do not readily form stable Se-HBs. Strong protic acids reverse the reaction, converting HBs back into HCs (see Scheme 2). Their reactive site is mainly position 2, and numerous reactions transform HCs into a wide range of heterocyclic[2,6,10,45,140,168] or acyclic[169] compounds (Scheme 14; for the sake of simplicity, the archetypal HC **17** is shown; the **17** → **72** transformation requires the air's O_2 to participate[81,170]).

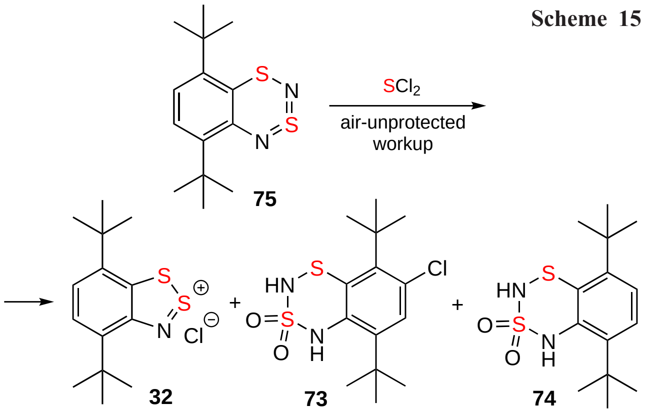
Scheme 14



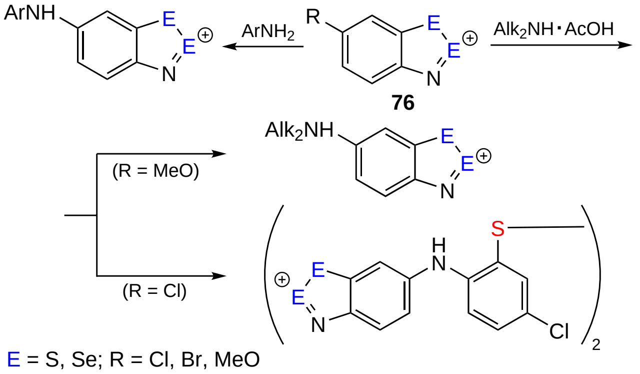
The HC **28** forms the Lewis-acid complex **28** $GaCl_3$.[40] The complex of HC **32** with S,S-dioxides **73**/**74** (Scheme 15) is formed by the reaction of dithiadiazine **75** with SCl_2 under air during the work up process. A putative precursor of **73**/**74** is RC $[\mathbf{75}]^{\bullet +}$ (*cf.* Ref. 171), formed by the oxidation of **75** with SCl_2, followed by chlorination and exposure to atmospheric O_2/H_2O during the work up.[103]

The carbocyclic reactivity of HCs is associated with nucleophilic substitution of Cl, Br, and MeO under the action of organic amines; the substitution rate depends on both the substituent and the chalcogen, with a particularly pronounced dependence on the chalcogen in position 2 mentioned above (Scheme 16).[2,6,106,172–175]

Scheme 15



Scheme 16



2.2. Radicals

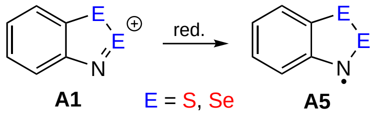
2.2.1. Reduction of cations

Numerous S- and Se-HRs have been obtained *via* reversible (electro) chemical reduction of their corresponding HCs (Scheme 17), which is the main approach to these Herz species. The chemical reduction agents used are usually Zn, Zn/Cu, Ph_3Sb, $[I]^-$, $FeCp_2$, $FeCp^*_2$, and tetrakis(dimethylamino)ethylene (TDAE); and the solvents are nonpolar hydrocarbons, *e.g.* heptane, cyclohexane, or benzene. The electrochemical potentials at a stationary Pt electrode are quite low, varying from –0.26 to 0.18 V *vs.* SCE; typical solvents are DME or MeCN. For the archetypal HC **17**, replacing the S atom at position 2 with a Se atom (HC **23**) causes an anodic shift of ~0.1 V, while there is no effect at position 1 (HC **26**); replacing two S atoms (HC **24**) shows a combined effect with the same ~0.1 V shift. The reduction is visually monitored by the change in color of the reaction mixtures (compared to HCs, HRs are deep-colored from red to green; see below) and the disappearing of the poorly soluble starting HSs (Refs 16, 18, 31–33, 35, 40, 81, 114, 127, 144, 145, 150–154, 162, 176–179). Reduction of Te HC **28** results in unidentified diamagnetic products.[40] Elemental halogens Cl_2 and Br_2 convert HRs back to HCs.[18]

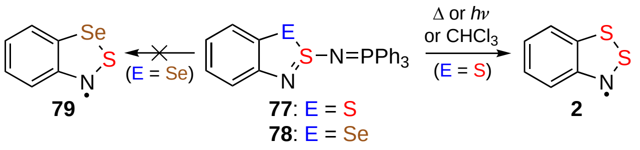
2.2.2. Ring modifications

HRs can be obtained by thermolysis of various precursors, *e.g.*, HBs (*cf.* **19** → **2**).[25,180] In the hydrocarbon and fluorocarbon series, compounds **77** transform into HRs upon thermolysis or

Scheme 17



Scheme 18

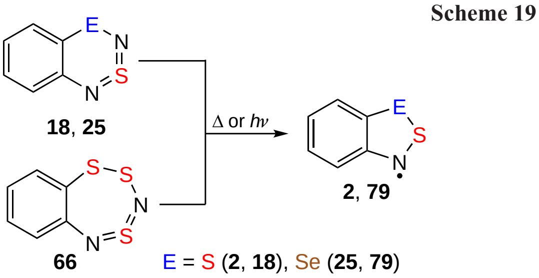


simply upon dissolution in $CHCl_3$. However, for their Se congener **78**, the corresponding HR **79** was not observed under the same conditions (Scheme 18).[181–183]

2.2.3. Ring contractions

Many HRs, including those inaccessible by other methods such as polyfluorinated ones, can be generated from dichalcogenadiazines **18** and **25** in dilute organic solutions by mild thermolysis or UV photolysis. This method also extends to trithiadiazepines **66** (Scheme 19). This approach is suitable for both EPR and mechanistic studies.[44,81,103,170,181,182,184–189]

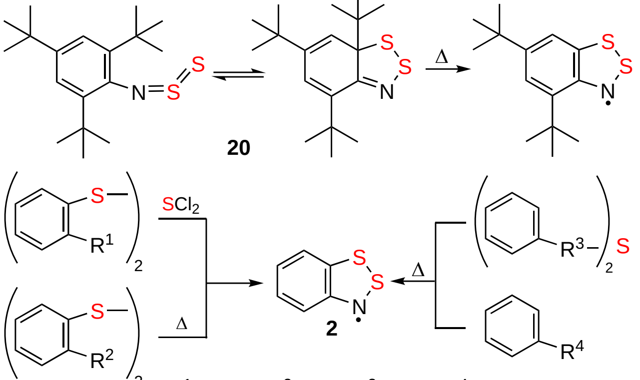
Scheme 19



2.2.4. Ring closures

N-thiosulfinyl **20** upon heating under anaerobic conditions eliminates $Bu^{t\bullet}$ and transforms to EPR-detected HR corresponding to HC **21**; thermolysis in air provides the corresponding HB and amine, and *p*-toluenesulfonic acid catalyst increases their yields. In addition, the ring closures towards HRs are EPR-observed for some other reactions of various acyclic sulfur-nitrogen derivatives (Scheme 20).[25,89,180,190,191]

Scheme 20

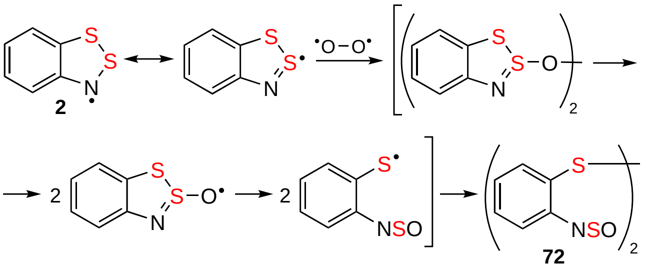


$R^1 = NH_2$; $R^2 = N_3$; $R^3 = NH$; $R^4 = N(SAlk)_2$

2.2.5. Reactivity

HRs are thermally stable, with benzo-annelated derivatives up to ~120–150°C. Above, various HQs and azaarenes are formed, *e.g.*, phenazine and derivatives, most likely by self-condensation of HRs *via* π dimers and some other transformations (see below).[2,12,25,33,44,81,89,117,182,183,191] HRs are unstable in protic solvents, as well as in those containing acidic admixtures. In particular, they decompose rapidly in $CHCl_3$ with the formation of an unidentified salt-like precipitate,[23] most likely caused by traces of HCl. Protected from H_2O/O_2 and UV light, HRs remain persistent in aprotic organic solutions at ambient temperature, and many HRs are isolated in a pure form (below). Reaction with O_2 involves recombination followed by heteroring-opening to form O=S=N-functionalized diaryl disulfides **72** (Scheme 21, the archetypal HR **2** is shown for simplicity; *cf.* Scheme 14).[81,170] The expected products of reacting with H_2O under unaerobic conditions are 1,2-aminothiols, *i.e.*, **16** and its derivatives. However, the corresponding protocols appear never to have been published, and in practice these compounds were used without isolation.

Scheme 21



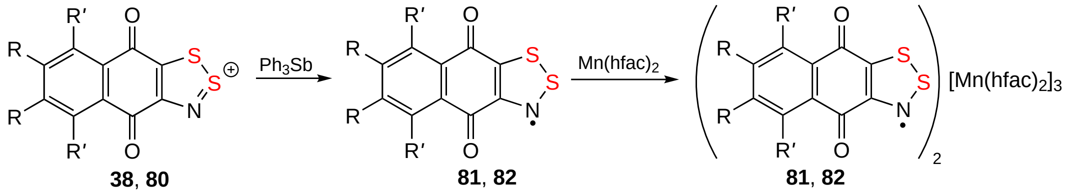
HRs exhibit electrochemical redox activity and are reversibly oxidised to HCs.[23] The oxidation potential depends on the chalcogen atom in position 2 (S or Se) and the working electrode material (Hg or Pt). Electrochemical reduction is irreversible, *e.g.*, for **2** and **79**.[30,40] 1,2-Naphthoquinone-based HR has stable cationic (*i.e.*, HC) and anionic (*i.e.*, naphthoxide) states.[114]

Furthermore, HRs are practically unexplored, but highly promising paramagnetic ligands for metal coordination compounds. In particular, HCs **38** and **80** were reduced to HRs **81** and **82**, which with $Mn(hfac)_2$ formed complexes $[HR]_2[Mn(hfac)_2]_3$ (Scheme 22) exhibiting an $S = 13/2$ ground state. In the complexes one Mn atom is bonded to two O atoms and each of two other Mn atoms is bonded to O and N atoms.[139]

2.3. Quinoids, bipolar ions and radical anions

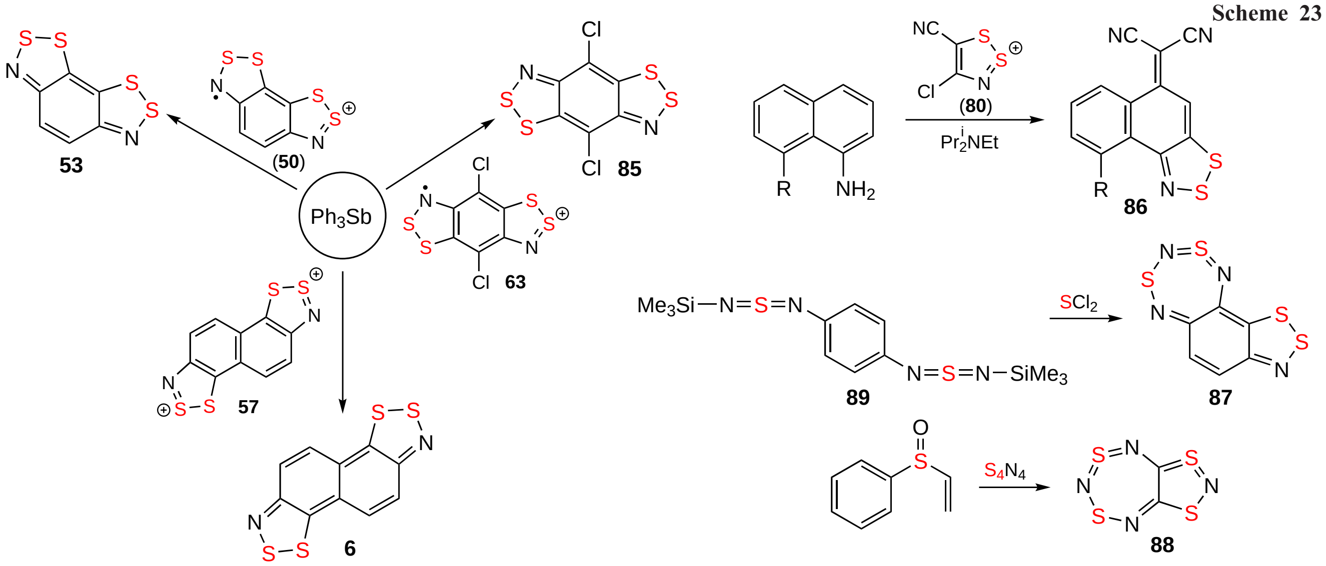
HQs (**A13**, **A14**, **6**–**10**, **83–86**; Figure 1 and Scheme 23) can be considered as 4*n* π-electron antiaromatics, singlet diradicals or bipolar ions;[31,32,39,65–68,192,193] as well as 4*n*+2 π-electron

Scheme 22

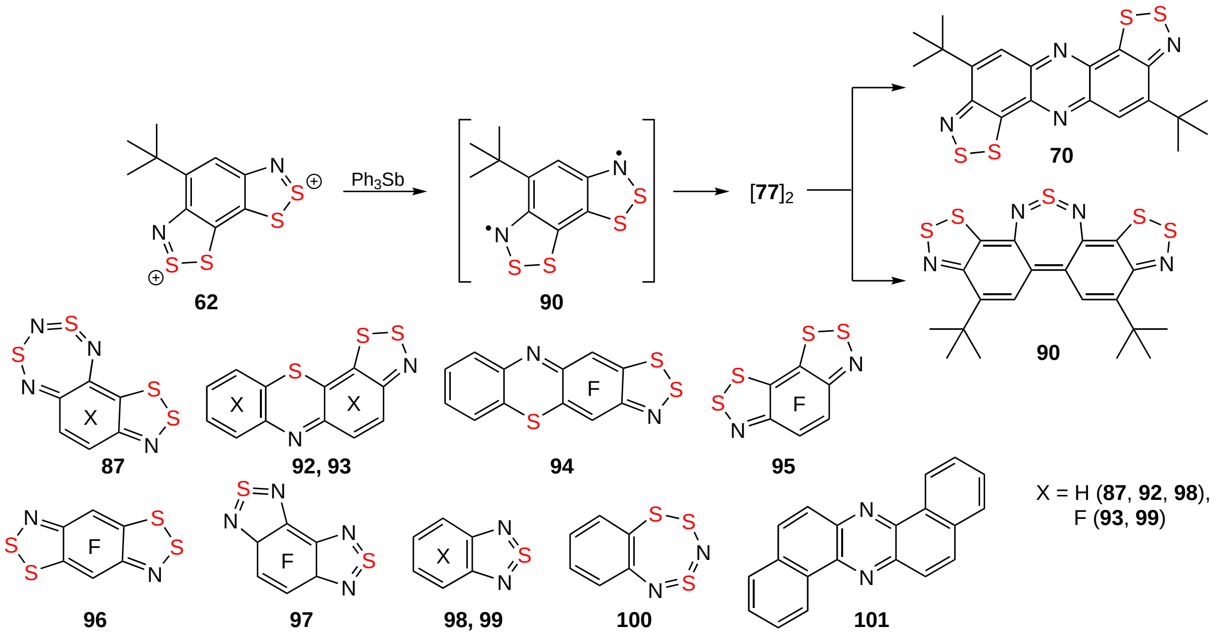


R = Me, R′ = H (**38**, **81**);
R = H, R′ = Me (**80**, **82**);
hfac is hexafluoroacetylacetonate

Scheme 23



Scheme 24

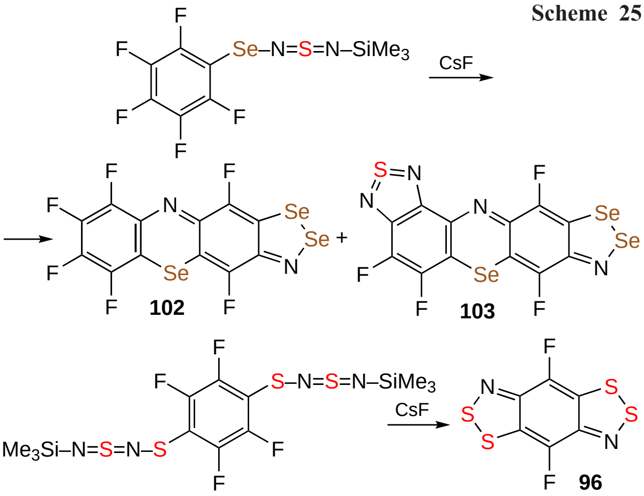


aromatics (**87**, *cf.* Wolmeshäuser-type quinoid **88**; Scheme 23).[166,194,195] They are typical for polysulfur-nitrogen chemistry in general.[59,60] In the hydrocarbon series, HQs are obtained by various methods, including carbocyclic nucleophilic substitution in HCs;[125,142,196] reduction of RCs/dications;[31,32,39] and miscellaneous reactions.[166,194,195,197] Compared to the isostructural phenazulene and azulene,[198] the quinoids **87** and **88** prepared from bis(sulfur diimide) **89** and SCl_2, and phenyl vinyl sulfoxide and $(SN)_4$, respectively (see Scheme 23), have reversed molecular polarization: the seven-membered ring bears a negative charge; and the five-membered ring a positive one.

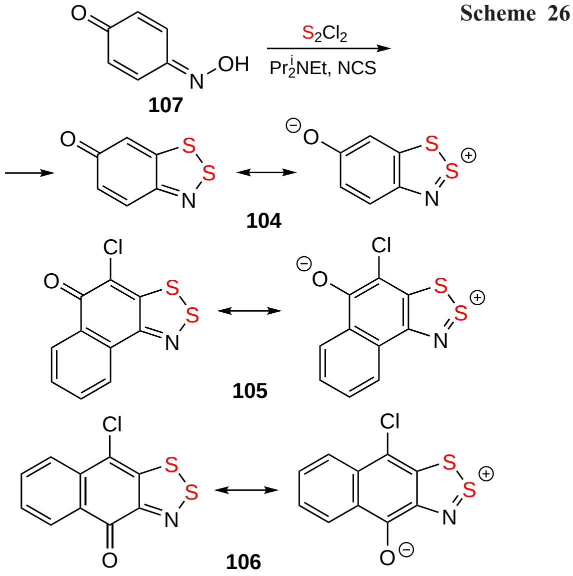
Importantly, HQs are also obtained by the self-condensation of HRs in concentrated solutions, as exemplified by the formation of **70** and **90** from diradical **91** *via* isomeric π dimers $[\mathbf{91}]_2$.[117] The similar structures of the hydro-/fluorocarbon scaffolds suggest that the self-condensation reactions leading to HQs **87** and **92**–**96** involve non-electrophilic/nucleophilic annulation processes, but rather radical ones. The isolation of other heterocycles, such as **66** and **97**–**101**, further reinforces the complexity of the involved transformations (Scheme 24).[2,12,25,33,44,81,117,182,183] In addition to HQs **92**–**97** from the self-condensation of HRs, fluorinated HQs **96**, **102**, and **103** are obtained from transformations of 1,3-C_6F_4(–S–N=S=N–$SiMe_3$)$_2$ and C_6F_5–Se–N=S=N–$SiMe_3$ under the influence of CsF (Scheme 25), together with other chalcogen-nitrogen π-heterocycles (*cf.* transformation **89** → **87**;[194] Scheme 23); and **93** is also found among the products of the reaction between tetrafluorinated dithiadiazine **18** and Ph_3As.[137]

Oximes allow extension of the Herz reaction to nonaromatic starting materials. In particular, hydrocarbon HQs and related S,O-bipolar ions have been synthesized from oximes in both aromatic (compounds **104**–**107**; Scheme 26) and nonaromatic (Scheme 27) series. In some cases with the nonaromatics, the presence of strong bases, such as Bu^i_3N or Pr^i_2NEt (Hünig's base), was requireded (Scheme 28). In some other cases, the assistance of NCS or Ph_3P was required (see Scheme 27). The reactions are often accompanied by carbocycle chlorination.[20,60,128,199–203]

Scheme 25



Scheme 26

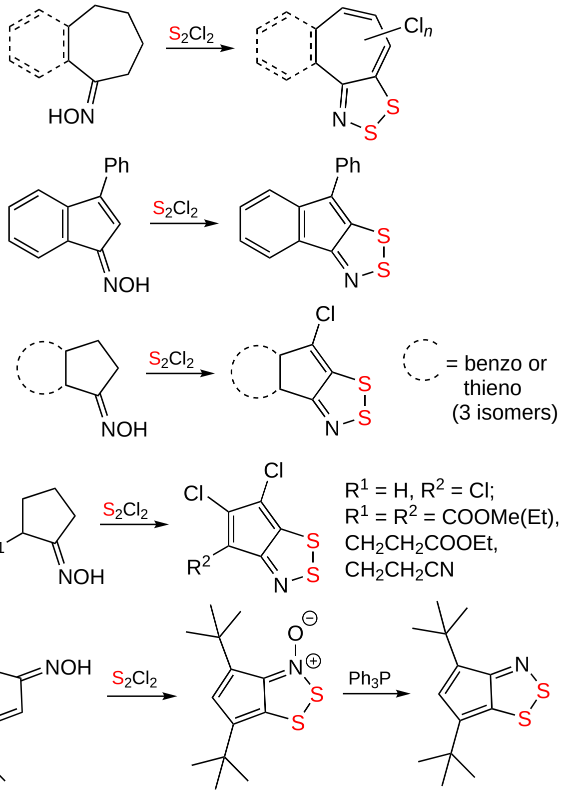


HQs **108**–**110** have also been obtained from neutral derivatives of AC and related compounds by miscellaneous reactions (Scheme 29).[80,204]

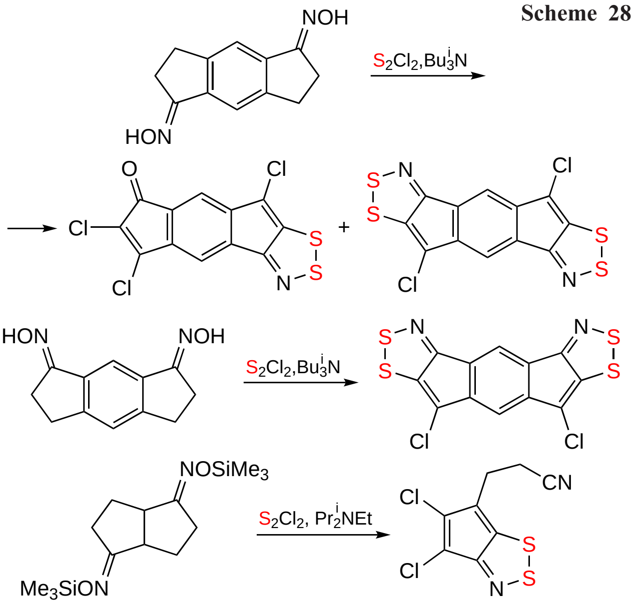
HQs exhibit selective S → Se chalcogen exchange in position 2. For example, S-HQs **111** transform into Se-HQs **112** under the influence of SeO_2 (Scheme 30). The exchange is thought to be thermodynamically-driven, as the SO_2 byproduct is more preferable than the starting SeO_2.[109,115,205] In particular, the incorporation of Se into heterocycles is a hot topic in current chemistry and biomedicine.[206]

The redox behavior of HQs depends strongly on their structure. HQ **70** produces persistent RA **15** (see Figure 1) under electrochemical reduction (Scheme 31) in addition to electrochemical oxidation to RC **14** (Scheme 13). HQ **84** forms persistent RA **113** on both chemical and electrochemical reduction; and its archetype **114** is isolated in the form of thermally stable salts. At the same time, HQs **105** and **115** do not afford the expected RAs **116** and **117** (see Scheme 31).[117,141,193,199,205] According to DFT calculations, the SOMO of RA of **118** (the nonhalogenated archetype of **85** and **98**) is strongly antibonding, which leads to cleavage of one on the S–N bonds with the formation of the acyclic structure of the $S^{(-)}\cdots N^{(\bullet)}$ type[39] (see below).

Scheme 27



Scheme 28

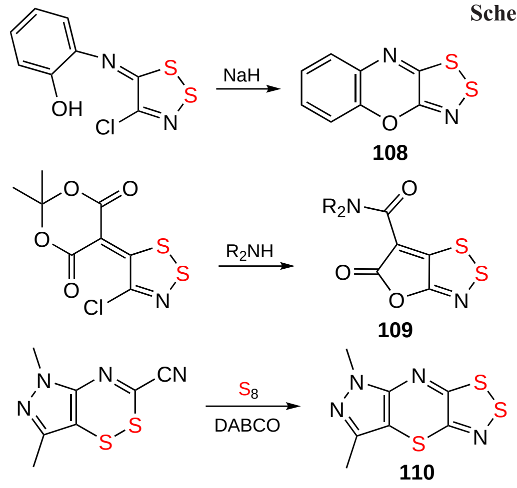


The S,O- and S,N-bipolar ions **7**–**10** are synthesized by deprotonation of HCs **119**–**121** with 1,8-di(dimethylamino)naphthaline (aka the proton sponge) which has a strong tendency to attract protons; the ion **122** is obtained from HC **123** through unstable HRs **124** and **125** (*cf.* **8**, **47**, **48**, and **67** for **9**, **119**–**121**, and **123**). Likewise, HR **126** transforms into bipolar ion **7** (Scheme 32); however, Se analogues of **124** and **126** do not undergo this transformation.[143,149,154,162,176,207,208]

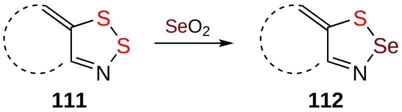
2.4. Bases

Mild thermolysis of HBs leads to EPR-detected HRs, which under harsher condidions yield phenazines (Scheme 33; here and below, the archetypes are shown for simplicity).[25,180,191] The mechanism of the first transformation is unclear, whereas

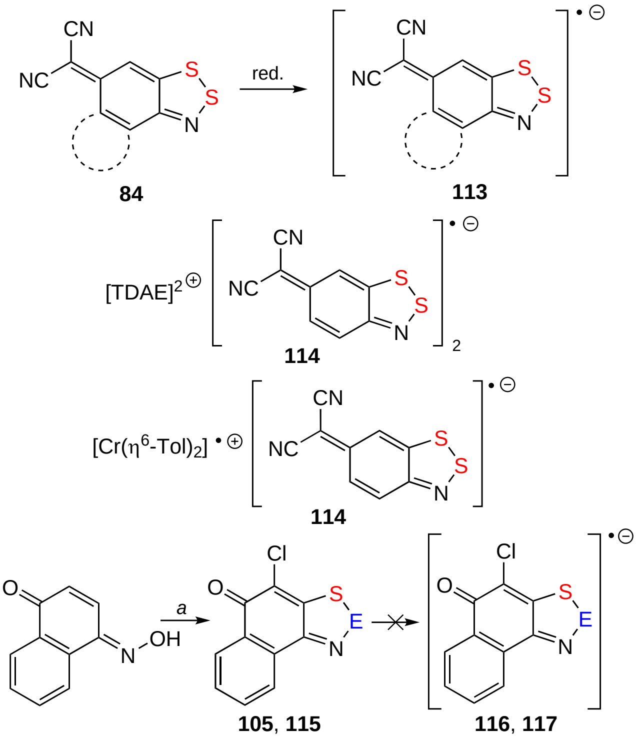
Scheme 29



Scheme 30

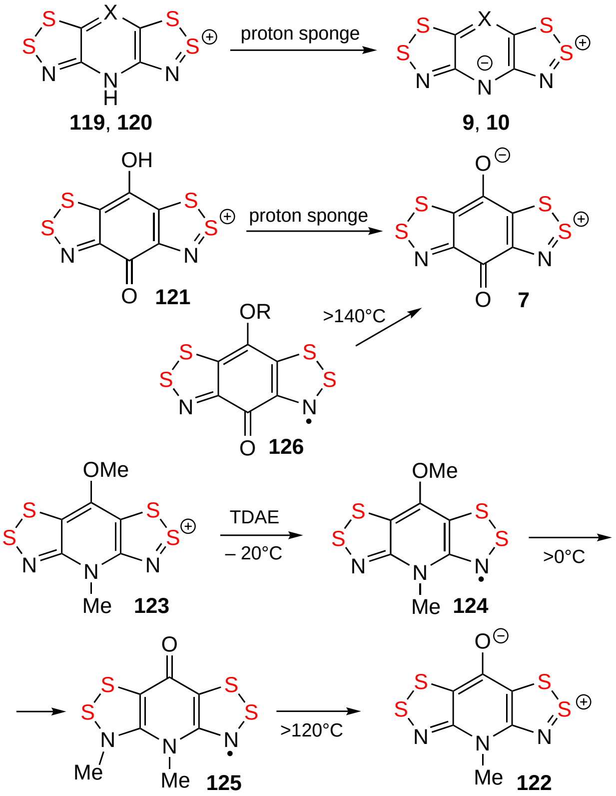


Scheme 31



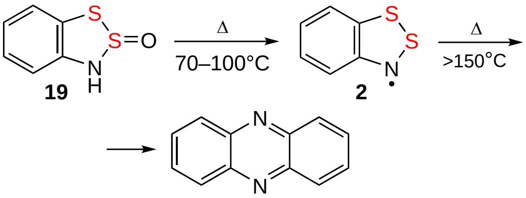
(*a*) S_2Cl_2, Se_2Cl_2, SeO_2; E = S (**105**, **116**), Se (**115**, **117**)

Scheme 32

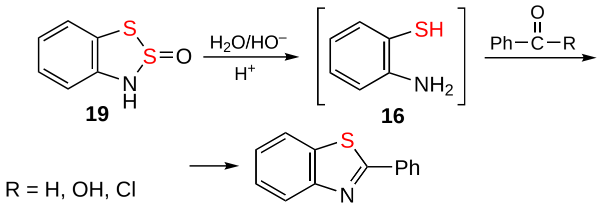


9, **119**: X = CH; **10**, **120**: X = N; **126**: R = Me, Ac

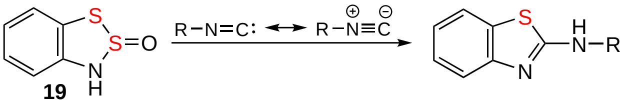
Scheme 33



Scheme 34



Scheme 35



for the second, π dimerization of HRs is proposed, followed by isomerization of the dimers and elimination of sulfur.[89]

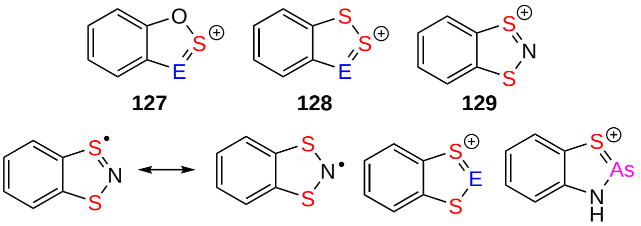
As mentioned above, strong protic acids convert HBs to HCs (see Scheme 2). Mild alkaline hydrolysis of HBs leads, after neutralization, to the formation of 1,2-aminothiols, *i.e.*, **16** and its derivatives, which are normally used without isolation for the synthesis of dyes (*i.e.*, thioindigo) and some other products, *e.g.*, benzothiazoles (Scheme 34; *cf.* Scheme 14).[2–4,6,7,10,104–106,140] The interaction of HBs with organic isocyanides also yields benzothiazoles (Scheme 35).[8]

2.5. Main-group expansion

Both fundamental and practical considerations motivate the further extension of Herz chemistry to include the lightest chalcogen oxygen (another unconventional element in this group) and the heavier pnictogens phosphorus and arsenic in the heterocyclic compounds, as well as the polyhalogenation of carbocyclic systems. Today, only a few polyhalogenated (F, Cl) HQs and bipolar ions are known in this context (Schemes 23–25).

DFT calculations suggest that HCs **127**, **128** and their Se analogues are quite feasible, as are the corresponding HRs.[137] In particular, the related WC and WR **129** and **130** are known,[88] and the former have P, As, and Sb congeners **131** and **132** (Scheme 36).[209–216] These findings suggest that S-oxides **133** (Ref. 217) (for monocyclic sulfamidites, see Ref. 47) could potentially be transformed into HCs **134** by strong protic acids. Furthermore, hydrocarbon[218,219] and fluorocarbon derivatives of the Ar–O–N=S=O motif could be converted into O containing Herz species **135**–**138** (Scheme 37) using well-established Herz chemistry methods.[44,165,166,182,185,220–223] These reactions could potentially be used to synthesize novel heterocyclic and carbocyclic compounds with diverse properties.

Scheme 36



127: E = N, P, As; **128**: E = P, As; **131**: E = P, As, Sb

In the carbocyclic context, where polyfluorinated HCs are unknown and EPR-observed HRs have not been isolated[44,81,188,189] (in contrast to WCs/WRs),[81,137,221,224,225] DFT calculations suggest that the archetypal HCs are HRs are thermodynamically more favored than the corresponding WC and WR by ~11 and ~14 kcal mol^{-1}, respectively. Tetrafluorination changes this thermodynamic balance only minimally.[224] Monofluorinated ArNH$_2$ undergo the Herz reaction, but the resulting HSs are transformed into 1,2,3-benzothiadiazoles without isolation.[10] Given the significant impact of (poly) halogenation of arenes, including those fused with π-heterocycles, on electronic structure, crystal packing, and electrical/magnetic properties,[225–232] (poly)halogenated HCs, HRs and HQs warrant further investigation.

3. Molecular and electronic structure

Chemical bonds are not directly observable and can only be conceptualized through theoretical descriptors.[233] For Herz chemistry, the various descriptors used throughout its history do not show consistent relationships even for the most relevant compound libraries, posing a significant challenge for further theoretical investigations. Over the years, numerous HCs, HRs, HQs, radical and bipolar ions, dications have been structurally defined by XRD, whereas HBs have only recently been characterized by this method. By EPR, HRs were initially assigned to 1,2-thiazetyls,[180,191] which was corrected with ^{33}S isotopomers.[18,26,27]

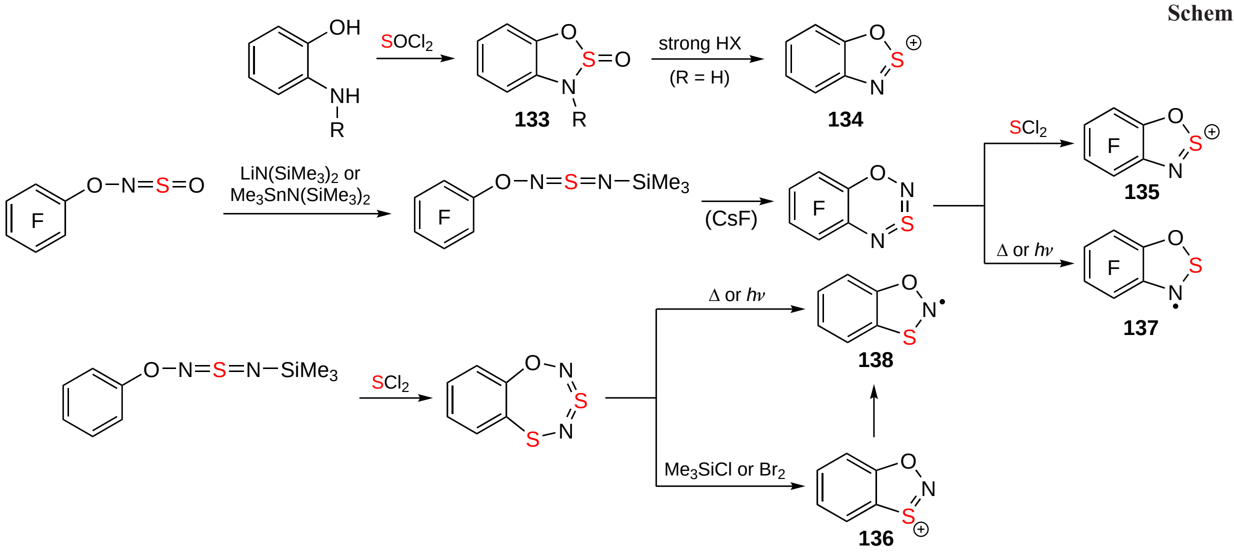
3.1. Cations and dications

According to XRD and quantum chemical calculations (Figures 2 and 3; Tables 1 and 2), HCs, RCs, and dications exhibit planar molecular scaffolds and delocalized π-systems[31–33,38–40,45,100,103,107,114,117,127,149,162,206,234–236] typical of unsaturated chalcogen-nitrogen heterocycles.[61,237] Structurally, HCs are rigid, and variations in the counterion only lead to minor alterations in their solid-state geometries. Gas-phase DFT calculations accurately reproduce the experimental geometries of HCs **17**, **23**, **24**, **26**, and **28**; ~60% of HC charge is localized on the heterocycles. Typical Hirshfeld atomic q values are ~0.23, 0.34 and –0.05 for S1, S2 and N3, respectively. The nucleus independent chemical shift (NICS) values of ~–6 and –15 for carbo- and heterocycles, respectively, suggest the aromaticity of HCs. At the same time, bonds C4–C5 and C6–C7 are shorter, and their bond orders are higher than other C–C bonds, implying a certain *ortho*-quinoid character of HCs. Replacing of S with Se significantly modifies the atomic charges and bond lengths/orders only at the involved and neighboring sites.[38,40,103,173]

The linear dications **64** and **152** also feature elongation of the heterocyclic C–C bonds prior to equalisation of all others, in contrast to the angular dication **62**. The XRD structure of the linear/angular dication **71**, known for three HCs with two counterions and two solvates, suggests that 1,2,3-dithiazoliums are structurally more rigid than benzene or pyrazine rings.[39,117]

Absorbance in UV-VIS and chemical shifts in heavier-nuclei NMR spectra of HCs are solvent and counter-ion dependent. The UV-VIS spectra of perchlorates in CF$_3$CO$_2$H reveal the λ_{max}

Scheme 37



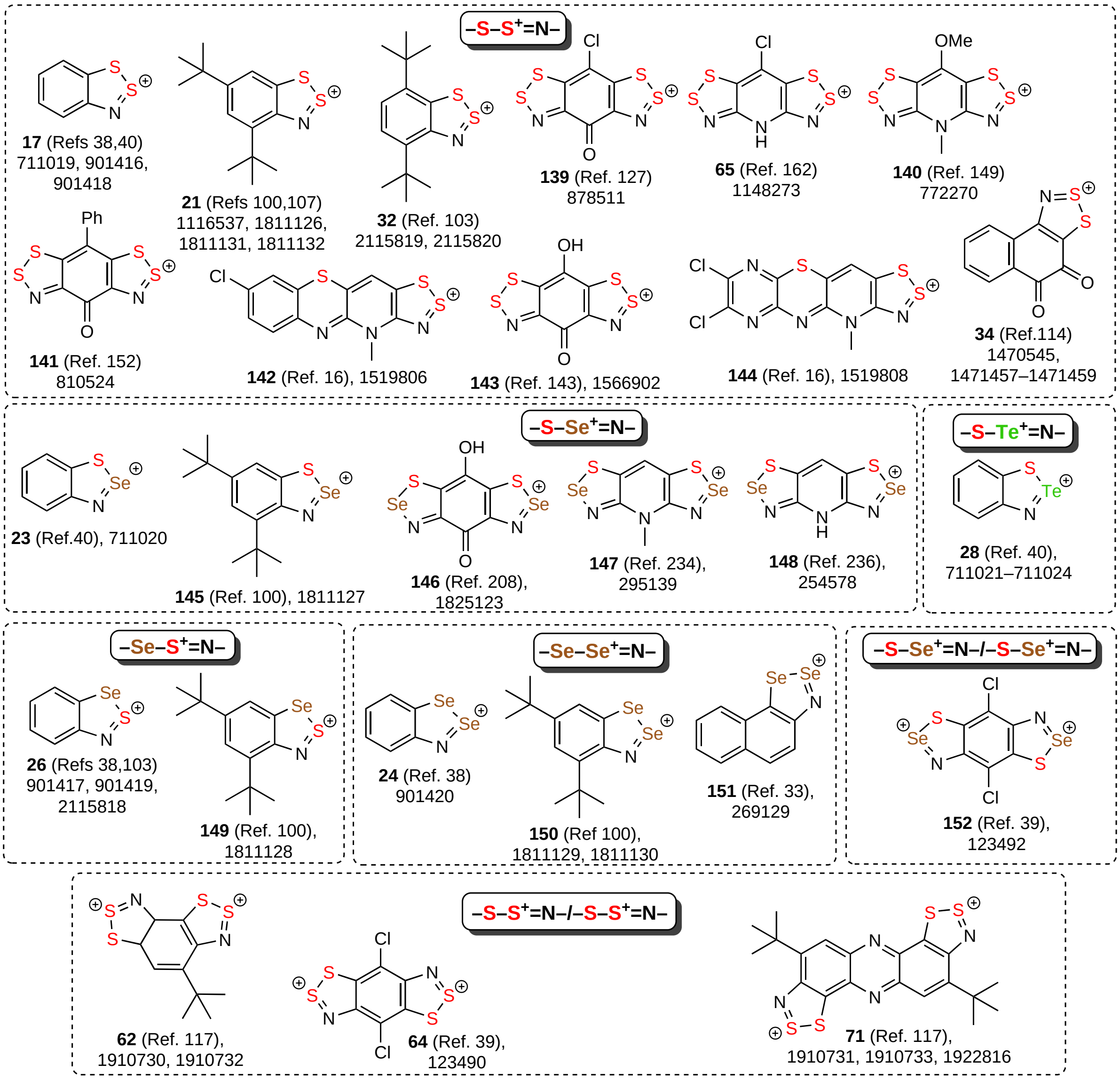


Figure 2. XRD-defined HCs and dications, and CCDC deposition numbers (here and below: multiple numbers for a given Herz species indicate different polymorphs or solvates, or temperatures of XRD measurements; and for charged species, also different counterions). Anions are $[Cl]^-$ for **21**, **26**, **32** (complex with **73**/**74**), **34**; $[TfO]^-$ for **28**, **34**, **62**, **71**, **141**–**144**, **147**; $[BF_4]^-$ for **17**, **26**; $[AlCl_4]^-$ for **64**, **152**; $[GaCl_4]^-$ for **17**, **23**, **24**, **28**, **34**; **62**, **71**; $[FeCl_4]^-$ for **34**; $[SbF_6]^-$ for **65**, **139**, **140**, **148**; $[SbCl_6]^-$ for **21**, **145**, **149**, **150**; $[SbCl_6]^-/[Cl]^-$ for **17**, **26**; $[TeCl_6]^{2-}$ for **150**; $[Te_2Cl_{10}]^{2-}$ for **28**; $[Te_3Cl_{14}]^{2-}$ and $[Te_4Cl_{18}]^{2-}$ for **21**; $[C_4F_9SO_3]^-$ for **146**.

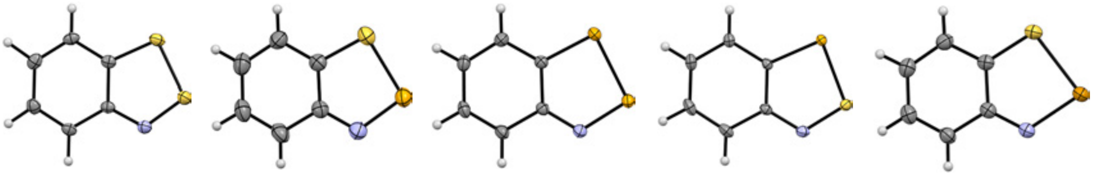

17 (Ref. 38) **23** (Ref. 40) **24** (Ref. 38) **26** (Ref. 103) **28** (Ref. 40)

Figure 3. XRD molecular structures of selected HCs; color code: C grey, H light grey, N blue, S yellow, Se light orange, Te dark orange.

bands in the range ~410–560. Substitution of S by Se at position 2 results in a bathochromic shift $\Delta\lambda_{max} \sim 20-25$[7,172,174] (Table 3). The spectra of the dications are quite similar to those of HCs, except for the UV-VIS spectrum of **62**, which has a λ_{max} of ~400.[117] The δ^{77}Se of Se-HCs falls within the downfield half of the window reported for Se–N compounds; and the δ^{77}Se for position 1 is upfield compared to the δ^{77}Se for position 2 (~1310–1420 and ~1470–1600, respectively). The DFT-calculated δ^{77}Se and δ^{15}N values are in reasonable agreement with the experiment, although δ^{77}Se is slightly underestimated; and δ^{15}N is overestimated[38,235] (Table 4).

3.2. Radicals and radical ions

XRD, EPR, and DFT studies (Figure 4 and Figure 5; Table 5 and Table 6) have confirmed that HRs and RCs have planar molecular geometries and delocalized π-systems. The (het)-arene-, *e.g.*, pyridine-, bridged HRs are resonance-stabilized in

Table 1. Selected bond lengths, and Hirshfeld bond orders and atomic charges of the archetypal HCs.[38,40,103]

HC	Anion	Bond, XRD			Atomic charge, DFT	
		bond [a]	length, Å	order	atom [a]	charge, e
17	$[BF_4]^-/[GaCl_4]^-$	C7*a*–S1	1.698/1.693	1.33	C7*a*	0.024
		S1–S2	2.028/2.024	1.21	S1	0.233
		S2–N3	1.577/1.561	1.70	S2	0.341
		N3–C3*a*	1.341/1.345	1.54	N3	–0.052
		C3*a*–C7*a*	1.428/1.437	1.23	C3*a*	0.069
26	$[BF_4]^-/[Cl]^-$	C7*a*–Se1	1.840/1.859	1.17	C7*a*	0.006
		Se1–S2	2.162/2.178	1.11	Se1	0.302
		S2–N3	1.587/1.589	1.72	S2	0.309
		N3–C3*a*	1.334/1.350	1.55	N3	–0.052
		C3*a*–C7*a*	1.424/1.428	1.26	C3*a*	0.064
23	$[GaCl_4]^-$	C7*a*–S1	1.711	1.34	C7*a*	0.024
		S1–Se2	2.174	1.13	S1	0.197
		Se2–N3	1.740	1.44	Se2	0.418
		N3–C3*a*	1.324	1.60	N3	–0.077
		C3*a*–C7*a*	1.422	1.22	C3*a*	0.066
24	$[GaCl_4]^-$	C7*a*–Se1	1.850	1.18	C7*a*	0.007
		Se1–Se2	2.290	1.08	Se1	0.267
		Se2–N3	1.742	1.45	Se2	0.384
		N3–C3*a*	1.330	1.60	N3	–0.079
		C3*a*–C7*a*	1.435	1.25	C3*a*	0.062
28	$[OTf]^-/[TeCl_5]^-/[GaCl_4]^-$	C7*a*–S1	1.702/1.698/1.702			
		S1–Te2	2.381/2.388/2.382			
		Te2–N3	1.954/1.954/1.954			
		N3–C3*a*	1.327/1.328/1.327			
		C3*a*–C7*a*	1.436/1.438/1.446			

[a] Heterocyclic numbering.

Table 2. Bond lengths (XRD, DFT) and Hirshfeld bond orders (DFT) for HC **17** and HR **2**.[38,40]

Bond [a]	**17**		**2**	
	length, DFT [b]/XRD [c], Å	order	length, DFT [b], Å	order
C7*a*–S1	1.698/1.693, 1.699	1.33	1.737	1.24
S1–S2	2.028/2.024, 2.034	1.21	2.087	1.11
S2–N3	1.577/1.561, 1.565	1.70	1.610	1.58
N3–C3*a*	1.341/1.345, 1.327	1.54	1.346	1.51
C3*a*–C7*a*	1.428/1.437, 1.434	1.23	1.417	1.32
C3*a*–C4	1.422/1.407, 1.412	1.37	1.404	1.43
C4–C5	1.362/1.352, 1.360	1.64	1.373	1.61
C5–C6	1.413/1.383, 1.412	1.40	1.394	1.51
C6–C7	1.372/1.357, 1.372	1.58	1.381	1.57
C7–C7*a*	1.409/1.397, 1.393	1.47	1.385	1.53

[a] Heterocyclic numbering. [b] B1B95/cc-pvqz. [c] $[BF_4]^-/[GaCl_4]^-$ salts.

Table 3. Selected UV-VIS data of Herz cations, radical cations and dications.[7,28,29,100,101,106,117,235,238,239]

HC	Solvent	λ_{max}, nm (logε)
$-S-S^{+}=N-$ [a]		
17	H_2SO_4	425 (3.29) or 430 (3.24)
6-H_3CO-**17**	H_2SO_4	470 (4.01) or 447 (3.87)
6-Cl-**17** (=**1**)	H_2SO_4	423 (3.60) or 427 (3.61)
17	CF_3CO_2H	426 (3.25)
4-H_3CO-**17**	CF_3CO_2H	551 (3.54)
6-H_3CO-**17**	CF_3CO_2H	439 (3.87)
14 [b]	THF	572 (4.34)
71	THF	408 (4.46)
$-S-Se^{+}=N-$		
23	H_2SO_4	450 (3.20)
6-Cl-**23**	H_2SO_4	450 (3.42)
6-H_3CO-**23**	H_2SO_4	475 (3.92)
145	$CHCl_3$	410 (4.05)
$-Se-S^{+}=N-$		
26	H_2SO_4	455 (3.28)
5-Cl-**26**	H_2SO_4	460 (3.20)
6-Cl-**26**	H_2SO_4	450 (3.45)
$-Se-Se^{+}=N-$		
24	H_2SO_4	470 (3.54)
6-Cl-**24**	H_2SO_4	470 (3.57)

[a] For spectra in graphical form, see Ref. 25. [b] For the corresponding dication, $\lambda_{max} \sim 410$ nm.[117]

that spin delocalization is enhanced by a resonance interaction between open- and closed-shell 1,2,3-dithiazole rings. The HC → HR transformation lengthens E–N bonds (E = S, Se), decreasing their bond orders, and markedly, but not completely, aligns C–C bonds (Refs 16, 31–38, 41, 42, 89, 110, 117, 126, 127, 139, 142–153, 155–157, 160, 176, 177, 192, 207, 234, 241–252 (see Table 5). According to the Bader analysis (QTAIM), this transformation significantly decreases the delocalization indices of the S–E bonds (E = S, N, C), exhibiting significant differences between HCs and HRs, with higher values for HCs; and the lowest calculated delocalization index

Table 4. Selected ^{15}N, ^{77}Se, and ^{125}Te NMR data of HCs.[25,38,40,100,101,240]

HC	Solvent	Anion	δ, ppm[a]	
			^{15}N	^{77}Se (^{125}Te)
–S–S$^+$=N–				
17	CD_3CN	$[BF_4]^–$	403.2	
		$[GaCl_4]^–$	388.7	
	CF_3CO_2H	$[Cl]^–$	406[b]	
5-I-**17**	CF_3CO_2H	$[Cl]^–$	401.7	
–S–Se$^+$=N–				
23	CD_3CN	$[GaCl_4]^–$		1556 or 1560
145	$CDCl_3$	$[Cl]^–$		1468
S1-**151**[c]	CD_3CN	$[GaCl_4]^–$		1536
–Se–S$^+$=N–				
26	$CF_3CO_2H/CDCl_3$, 4 : 1	$[Cl]^–$	425[b]	1410
	CD_3CN	$[GaCl_4]^–$	421[b]	1423
149	$CDCl_3$	$[Cl]^–$		1385
S2-**151**[d]	CD_3CN	$[GaCl_4]^–$		1400
–Se–Se$^+$=N–				
24	$CF_3CO_2H/CDCl_3$, 4 : 1	$[Cl]^–$	459.3	1581, 1344
	CD_3CN	$[GaCl_4]^–$	454.3	1601,[e] 1350[e,f]
150	$CDCl_3$	$[Cl]^–$		1492, 1314
		$[TeCl_6]^{2–}$		1504, 1312
151	CD_3CN	$[GaCl_4]^–$		1561, 1324
–S–Te$^+$=N–				
28	CD_3CN	$[GaCl_4]^–$		(1427)

[a] Standards: NH_3 (liq.), Me_2Se and Me_2Te. [b] ^{14}N NMR. [c] Naphtho[1,2-*d*][1,2,3]thiaselenazolium. [d] Naphtho[1,2-*d*][2,1,3]-thiaselenazolylium. [e] $J(^{77}Se–^{77}Se)$: 356 Hz. [f] $J(^{13}C7a–^{77}Se1)$: 152 Hz.

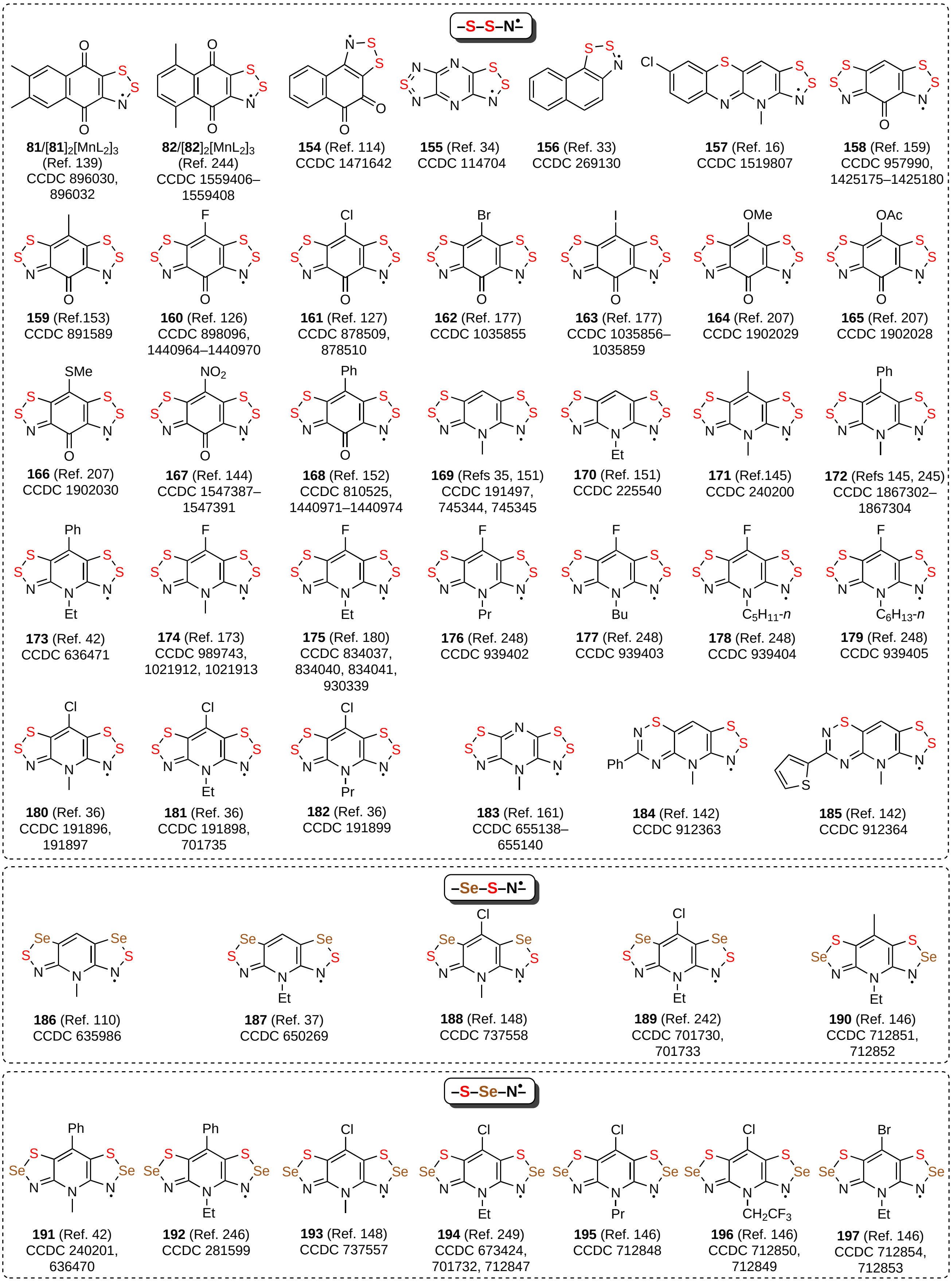
of 0.96 corresponds to the internal S···S bond in σ-dimer **153** (*cf.* with 1.35 for Me–S–S–Me).[253] This transformation also reduces the q values for all atoms, in particular by ~0.2–0.3 for the N and E atoms (E = S, Se) and ~0.1 for the C6 atom. For the N atoms, q is negative, whereas for the chalcogen atoms it is positive; for the latter, q is larger at position 2 than at position 1. The overall charges of the carbocycles and heterocycles of HRs are negligible.[38]

Resonance-stabilized HRs **A6** and **A7** (E = S, Se) are dimorphic, existing in two different molecular and crystal paramagnetic/diamagnetic modifications consisting of individual molecules and, in the space group $P2_1/c$, *e.g.*, the same as for $(SN)_x$,[256] unusual centrosymmetric σ-dimers, respectively.[147,150,160,176,243,247] The peculiarity of the dimers **153** and **206–209** is the hypervalent four-centre six-electron E–E···E–E (E = S, Se) bonds. A characteristic of these nearly linear bonds is that the terminal E–E distances, corresponding to the sum of covalent radii, are shorter than the internal E···E distance which is intermediate between the sums of covalent and van der Waals (VdW) radii, whereas the C–E distance is intermediate between those for the C–E single and C=E double bonds (Table 7; to emphasize this, the pseudo-quinoidal C=E designation is used for the σ-dimers in Figure 4 and Table 7). At normal pressure and temperatures below 400 K, dimers **204** do not undergo thermal dissociation **204** → 2(**174**); when exposed to external pressure at ambient temperature, they remain intact up to 8 GPa. The dimers **205**, however, undergo the **205** → 2(**175**) topochemical dissociation at 0.8 GPa. Dissociation of **204**/**205** can be induced by visible light of 650 nm, and the photoinduced HR pairs persist up to 150/242 K for HRs **174**/**175**, respectively, before reverting to the dimer states. Arrhenius activation energies for the HR ↔ σ-dimer interconversion are 8.3 and 19.6 kcal mol$^{–1}$ for 2(**174**) ↔ **204** / 2(**175**) ↔ **205**, respectively. DFT and CASSCF calculations suggest that the ground-state interconversion is symmetry-forbidden, requiring a configurational change $(\sigma_2^+)^2 \leftrightarrow (\pi)^+(\pi)^–$, but is allowed photochemically.[150,176,249] With pyrazine linkage, σ-dimers **153** and **210** exhibit bimodal

Table 5. Selected bond lengths, Hirshfeld bond orders and atomic charges, atomic spin densities and hfc constants (a) of HRs **A5** (Figure 1) from B1B95/cc-pvqz calculations.[38]

A5	Bond[a,b]			Charge[a]		Spin density and a constant		
2, E1 =E2 = S	C7*a*–S1	1.737	1.24	C7*a*	–0.021	S1	0.148	0.341
	S1–S2	2.087	1.11	S1	0.024	S2	0.287	0.450
	S2–N3	1.610	1.58	S2	0.105	N3	0.331	0.491
	N3–C3*a*	1.346	1.51	N3	–0.162	H4	0.004	–0.306
	C3*a*–C7*a*	1.417	1.32	C3*a*	0.031	H5	–0.001	0.096
						H6	0.007	–0.357
						H7	–0.002	0.098
						C7*a*	0.084	–
						C3*a*	–0.002	–
79, E1 = Se, E2 = S	C7*a*–Se1	1.878	1.09	C7*a*	–0.034	Se1	0.149	–
	Se1–S2	2.226	1.02	Se1	0.058	S2	0.289	0.424
	S2–N3	1.608	1.60	S2	0.083	N3	0.330	0.497
	N3–C3*a*	1.344	1.52	N3	–0.158	H4	0.004	–0.314
	C3*a*–C7*a*	1.417	1.34	C3a	0.031	H5	–0.001	0.109
						H6	0.007	–0.365
						H7	–0.002	0.110
						C7*a*	0.088	–
						C3*a*	–0.009	–
79, E1 = S, E2 = Se	C7*a*–S1	1.738	1.24	C7*a*	–0.021	S1	0.142	0.341
	S1–Se2	2.213	1.05	S1	0.001	Se2	0.265	–
	Se2–N3	1.766	1.33	Se2	0.152	N3	0.349	0.495
	N3–C3*a*	1.343	1.55	N3	–0.178	H4	0.004	–0.312
	C3*a*–C7*a*	1.738	1.24	C3a	0.028	H5	–0.001	0.105
						H6	0.007	–0.374
						H7	–0.002	0.111
						C7*a*	0.093	–
						C3*a*	–0.005	–
79, E1 = E2 = Se	C7*a*–Se1	1.881	1.09	C7*a*	–0.034	Se1	0.144	–
	Se1–Se2	2.342	1.01	Se1	0.037	Se2	0.266	–
	Se2–N3	1.764	1.35	Se2	0.127	N3	0.345	0.497
	N3–C3*a*	1.341	1.56	N3	–0.176	H4	0.004	–0.318
	C3*a*–C7*a*	1.419	1.34	C3a	0.028	H5	–0.002	0.115
						H6	0.007	–0.380
						H7	–0.002	0.120
						C7*a*	0.096	–
						C3*a*	–0.007	–

[a] Heterocyclic numbering. [b] Heterocycle/carbocycle (the sum exceeds 1 since C3*a* and C7*a* participate in both rings): E1 = E2 = S (**2**), 0.843/0.233; E1 = Se, E2 = S (**79**), 0.848/0.223; E1 = S, E2 = Se, 0.844/0.244; E1 = E2 = Se, 0.844/0.246..



–S–S–N$^\bullet$–

81/[**81**]$_2$[MnL$_2$]$_3$ (Ref. 139) CCDC 896030, 896032

82/[**82**]$_2$[MnL$_2$]$_3$ (Ref. 244) CCDC 1559406–1559408

154 (Ref. 114) CCDC 1471642

155 (Ref. 34) CCDC 114704

156 (Ref. 33) CCDC 269130

157 (Ref. 16) CCDC 1519807

158 (Ref. 159) CCDC 957990, 1425175–1425180

159 (Ref.153) CCDC 891589

160 (Ref. 126) CCDC 898096, 1440964–1440970

161 (Ref. 127) CCDC 878509, 878510

162 (Ref. 177) CCDC 1035855

163 (Ref. 177) CCDC 1035856–1035859

164 (Ref. 207) CCDC 1902029

165 (Ref. 207) CCDC 1902028

166 (Ref. 207) CCDC 1902030

167 (Ref. 144) CCDC 1547387–1547391

168 (Ref. 152) CCDC 810525, 1440971–1440974

169 (Refs 35, 151) CCDC 191497, 745344, 745345

170 (Ref. 151) CCDC 225540

171 (Ref.145) CCDC 240200

172 (Refs 145, 245) CCDC 1867302–1867304

173 (Ref. 42) CCDC 636471

174 (Ref. 173) CCDC 989743, 1021912, 1021913

175 (Ref. 180) CCDC 834037, 834040, 834041, 930339

176 (Ref. 248) CCDC 939402

177 (Ref. 248) CCDC 939403

178 (Ref. 248) CCDC 939404

179 (Ref. 248) CCDC 939405

180 (Ref. 36) CCDC 191896, 191897

181 (Ref. 36) CCDC 191898, 701735

182 (Ref. 36) CCDC 191899

183 (Ref. 161) CCDC 655138–655140

184 (Ref. 142) CCDC 912363

185 (Ref. 142) CCDC 912364

–Se–S–N$^\bullet$–

186 (Ref. 110) CCDC 635986

187 (Ref. 37) CCDC 650269

188 (Ref. 148) CCDC 737558

189 (Ref. 242) CCDC 701730, 701733

190 (Ref. 146) CCDC 712851, 712852

–S–Se–N$^\bullet$–

191 (Ref. 42) CCDC 240201, 636470

192 (Ref. 246) CCDC 281599

193 (Ref. 148) CCDC 737557

194 (Ref. 249) CCDC 673424, 701732, 712847

195 (Ref. 146) CCDC 712848

196 (Ref. 146) CCDC 712850, 712849

197 (Ref. 146) CCDC 712854, 712853

Figure 4. XRD-defined HRs, σ-dimers, and RCs, and their CCDC deposition numbers. Anions are [Cl]$^-$ for **49**; [ClO$_4$]$^-$ for **50**, **211** (for [**211**]$_3$[ClO$_4$]$_2$); [BF$_4$]$^-$ for **49**; [GaCl$_4$]$^-$ for **14**, **49**, **63**; [GaBr$_4$]$^-$ for **63**; [FSO$_3$]$^-$ for **50**; [TCNQ]$^{\bullet-}$ for **49**. L = hfac.

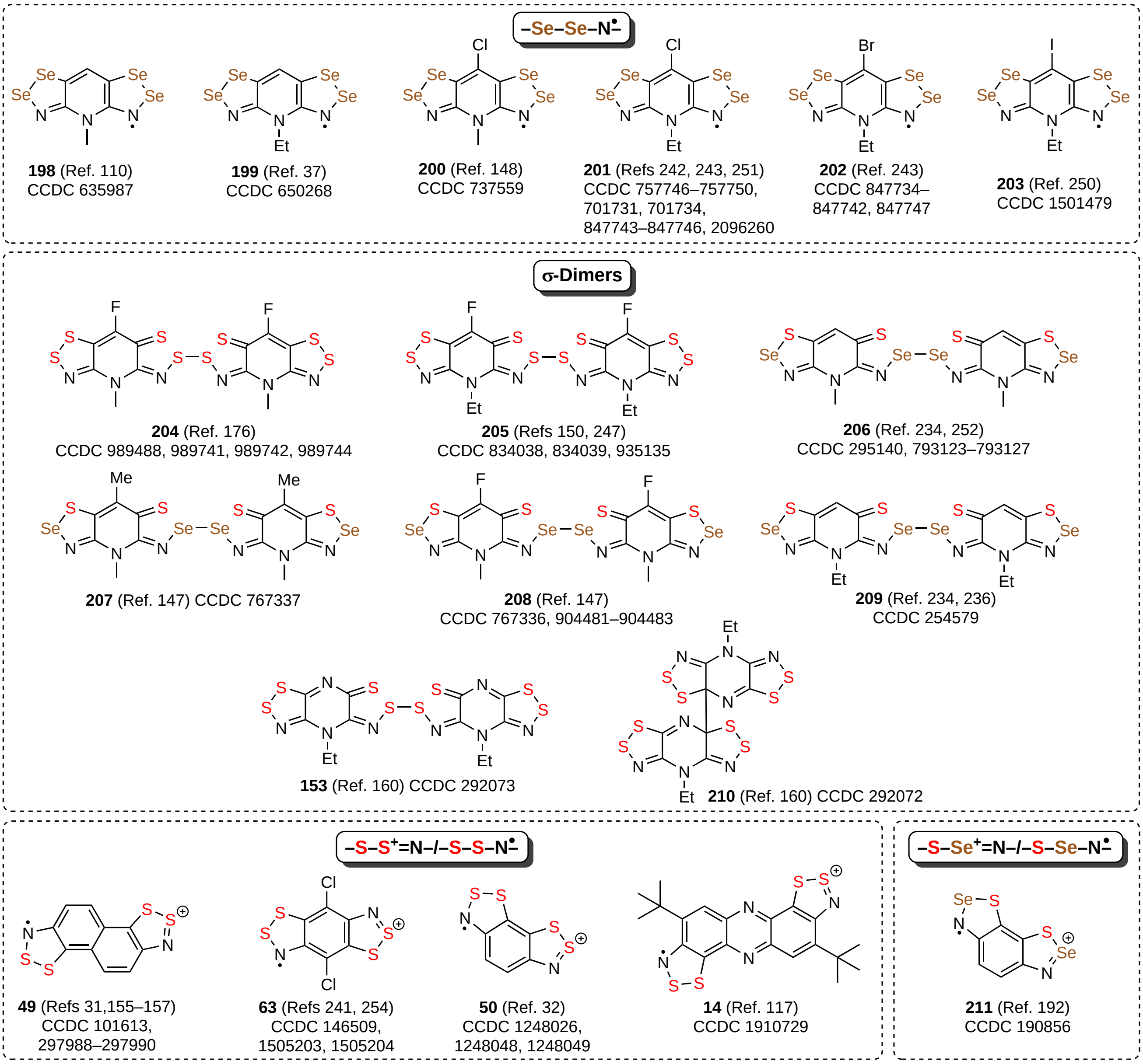


Figure 4 (continued). XRD-defined HRs, σ-dimers, and RCs, and their CCDC deposition numbers. Anions are $[Cl]^-$ for **49**; $[ClO_4]^-$ for **50**, **211** (for $[\mathbf{211}]_3[ClO_4]_2$); $[BF_4]^-$ for **49**; $[GaCl_4]^-$ for **14**, **49**, **63**; $[GaBr_4]^-$ for **63**; $[FSO_3]^-$ for **50**; $[TCNQ]^{\bullet-}$ for **49**. L = hfac.

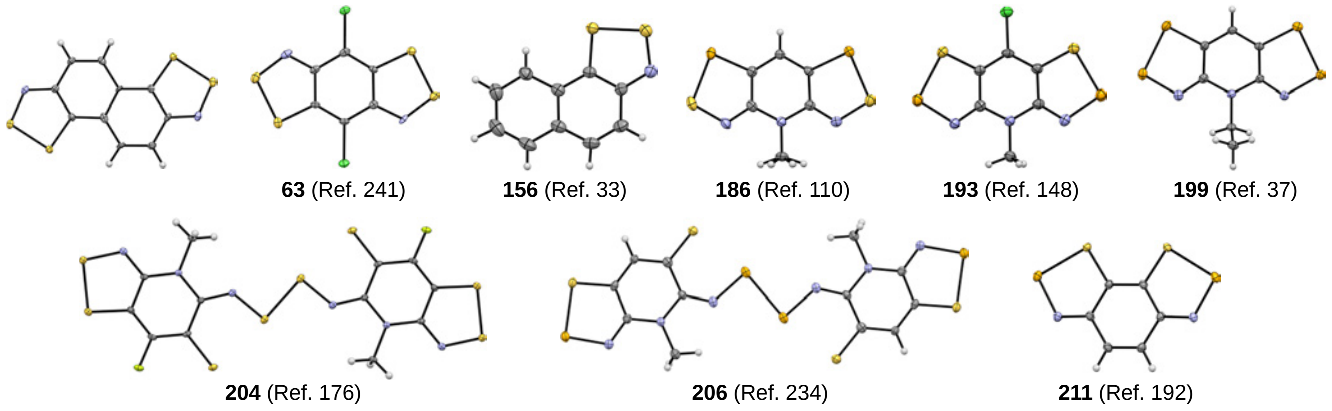


Figure 5. XRD molecular structures of selected HRs, σ-dimers, and RCs; color code: C grey, H light grey, Cl green, F light green, N blue, S yellow, Se light orange.

Table 6. Selected experimental *a* and *g* values of HRs **A5** (Figure 1) and their R4–R7 tetrafluoro derivatives.[18,25–27,38,40,41,185,255]

A5	*a*, mT[a]					*g*
	N3	R4	R5	R6	R7	
E1 = E2 = S (**2**)[a]	0.82	0.29	0.08	0.37	0.10	2.0080
F_4 derivative	0.82	0.57	0.26	1.00	0.35	2.0078
E1 = Se, E2 = S (**79**)[b]	0.93	0.30	0.09	0.35	0.10	2.0189
F_4 derivative	0.80	0.59	0.28	0.96	0.35	2.0140
E1 = S, E2 = Se (**A5**)	0.84	0.31	0.11	0.39	0.11	2.0116
E1 = E2 = Se[b] (**A5**)	0.97	0.30	0.10	0.39	0.11	2.0276

Note. For a compilation of EPR parameters of all-S HRs, see Ref. 89. [a] In ^{33}S isotopomer of 4,6-(Bu^t)$_2$ derivative of **2**, *a* constants for S1 and S2 are 0.37 and 0.45, respectively. [b] Constants *a* are measured with pulse EPR and ENDOR techniques in $CHCl_3$ at 30 K.

Table 7. Selected bond distances[a] in σ-dimers[147,150,160,176,234,236,252] of HRs at normal pressure.[b]

σ-Dimer, E	Bond distance, Å		
	C–S[c]	S–E	E···E
153, S	1.641	2.817	2.168
204, S	1.670	2.797	2.169
205, S	1.675	2.794	2.169
206, Se	1.694	2.785	2.460
207, Se	1.690	2.782	2.530
208, Se	1.694	2.790	2.565
209, Se	1.679	2.785	2.463

[a] The sums of covalent radii,[257] C–S 1.78, S–S 2.10, S–Se 2.25, Se–Se 2.40; the sums of VdW radii,[258] C···S 3.66, S···S 3.78, S···Se 3.71, Se···Se 3.64 Å. XRD statistical means for the bonds, C–S 1.75, C=S 1.64 Å.[259] [b] Interatomic distances of the hypervalent four-centre six-electron E–E···E–E (E = S, Se) bonds in σ-dimers of HRs depend on external pressure. [c] Comparable with the C=S distance in thioureas.[260]

association characterized by the presence of S–S and C–C bonds, respectively; **210** is kinetically, and **153** thermodynamically, favored. Replacing the N–Et group of **153**/**210** with N–Me gives non-dimerized **183**.[160,161]

The antibonding π*-SOMO (Figure 6) shows isolobal behavior for S and Se incarnations of HRs. The spin densities are mainly concentrated on the chalcogen-nitrogen fragments, especially at the N atoms. In **2** and its analogues, only ~23% of the spin density is transferred to the carbocycle, presumably encompassing atoms C4, C6 and C7a, similar to the spin density distribution observed in benzyl radicals. The substitution of S by Se introduces minor perturbations in the electronic structures, including spin density distributions and *a* magnitudes, primarily affecting neighbouring sites. Due to the strong spin-orbit coupling (SOC, which scales with the atomic number *Z* as Z^4)[261,262] at Se atoms and the large anisotropy of *g* tensors, the resulting EPR spectra in solution are significantly affected, sometimes becoming unresolved. In contrast to MP2 calculations, DFT simulations using B1B95 and B3LYP functionals (but not PBE) and 6-31G and cc-pvtz basis sets provide reasonable approximations of experimental *a* constants magnitudes (see Table 6).[33,38,40–42,45,81,88,125,182,185,189,236,244]

The UV-VIS spectra of isostructural HRs/HCs exhibit remarkable shape similarity; the HCs → HRs transformation primarily induces bathochromic shifts in λ_{max} (Tables 3 and 8) and modulates the fine structures of bands.[18,23,25,41,170,179] In particular, the spectra of HRs **2** and **156** show three solvent-dependent absorption bands that increase in intensity from long to short wavelengths; and the longest wavelength band of **2**, a fine structure with four maxima spaced at distances of ~400 cm^{-1}.[179]

High-spin HRs have only been investigated theoretically, where the quantitative estimation and interpretation of spin-energy gaps of polyradicals remains challenging.[264] For proposed diradicals **212** and **213** (Scheme 38), CASSCF and DFT simulations indicate that the ring closure mode and the nature and positions of chalcogen atoms influence the sign/magnitude of the singlet-triplet splitting ΔE_{ST}. The ground state

Table 8. Selected UV-VIS data of HRs.[41,170]

HR	Solvent	λ_{max}, nm
2	Cyclohexane/benzene	~500/520
4,6-Bu$^t_2$-**2**	Hexane	~520[a]
152	Cyclohexane	~600

Note. For spectra in graphical form, see refs.[23,25,170,179,263] [a] Two other bands at ~385 and 344 nm.

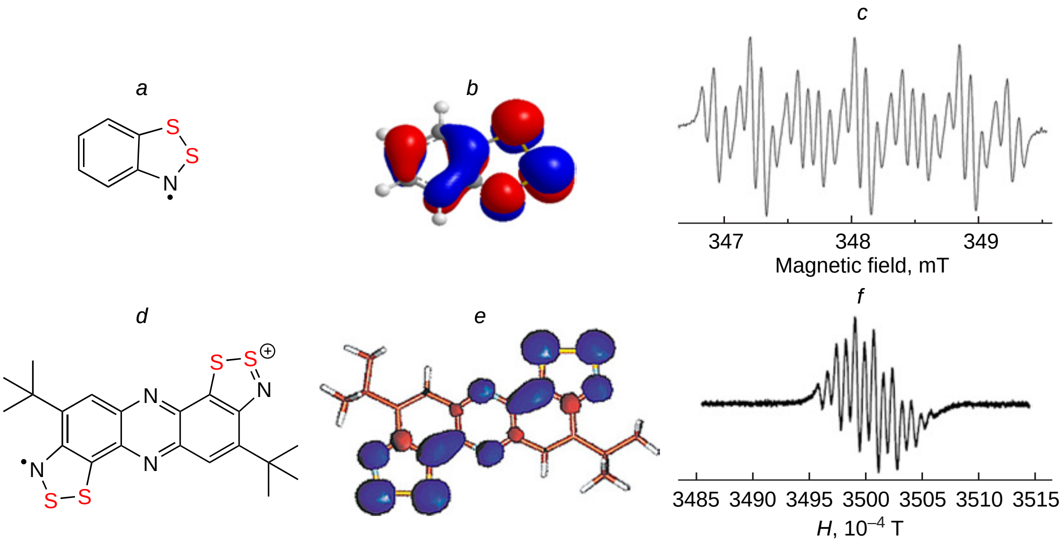
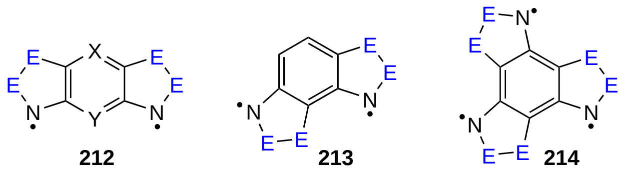


Figure 6. The π*-SOMO and solution EPR spectrum of HR **2** (top) and RC **14** (bottom). Experimental hfc constants *a* (mT): **2**: 0.82 (a_N), and 0.37, 0.24, 0.10, 0.08 (a_H);[38] **14**: 0.16 (a_N, dithiazole), 0.08 (a_N, phenazine), 0.01 (a_H, phenazine).[117]

Scheme 38



212 **213** **214**

E = S, Se; for S-PX **212**: X = C–H, C–R, N; Y = C–H, N

of the all-S linear radical **212** is a singlet. Replacing S with Se decreases the absolute value of ΔE_{ST} and results in a triplet ground state for the all-Se derivative.[81,88] Electron-donating substituents in the central ring stabilize the paramagnetic state of all-S **212** and its aza-congeners; while electron-withdrawing substituents stabilize the diamagnetic bipolar state.[177,265] For angular diradicals **213**, irrespective of S and Se combinations, the ground state is a triplet with a much larger ΔE_{ST} compared to linear **212**. For C_3-symmetrical angular triradicals **214**, CASSCF/DFT calculations propose a quartet ground state. Replacing S with Se has a negligible impact on the doublet-quartet splitting, with two doublet states nearly degenerate.[81,88,265,266]

Similar to HCs/HRs, RCs **14**, **49**, **50**, **63**, and **211**[31,32,117,155–157,192,241] and RAs **15**, **113**, and **114**[141,196,199] exhibit π-delocalization (Figures 6–8). In **113** and **114** the spin density and negative charge are distributed throughout the molecule; but the density has a higher concentration on the heterocyclic moieties. Persistent RAs **113** and **114** are chromophores with λ_{max} values of ~660 (for neutral precursors M, λ_{max} values are ~575); and **15** (Figure 7) is a NIR chromophore with λ_{max} ~1000.[117] In the transformation from M to RA, DFT calculations indicate the lengthening of the heterocyclic S–E (E = C, N, S) and N–C bonds, accompanied by a shortening of the C–C bond, reflecting the antibonding character of the π*-SOMO (see Figure 7; *cf.* HCs/HRs). For **114**, the archetype of RAs **113**, magnetic properties of the radical-ion salt $[Cr(\eta^6\text{-}Tol)_2][\mathbf{114}]$ suggest its solid-state π dimerization.[141,196,199] Compared to **15** and **113**, RAs **116** and **117** (see Scheme 31) are highly unstable. DFT calculations on the related RA **215** and its Se congener suggest a σ*-SOMO with an abnormally elongated S···E (E = S, Se) distance (Figure 8), *i.e.*, weakening or breakage of the corresponding bond[205] (*cf.* RA **118**).[39]

3.3. Quinoids and bipolar ions

The stereoelectronic properties of HQs are varied. Structurally characterized HQs (Figures 9 and 10) show localized double and single bonds. Some HQs are formally antiaromatic, which can also be assigned to singlet diradicals in the diamagnetic ground state, while others are formally aromatic, *e.g.*, **87** and **216**. For HQ **118**, DFT calculations suggest that the excited triplet state is 0.74 eV higher in energy than the singlet ground state; conversely, for its 1,3,2-isomer, the triplet ground state is 0.48 eV lower in energy than the singlet state. The bonding situation in many HQs can be represented by superposition of nonpolar and bipolar structures, *i.e.*, of S,O/S,N-bipolar ions, with the charge differentiation arising from the separation of the π-system into two distinct subunits (Figure 9).[31,32,39,65–67,85,114,117,128,141,149,162,192,193,199,200,267]

HQs exhibit chromophoric properties with λ_{max} ~ 460–660.[31,32,39,183,194,200] In particular, 6-6-5 tricyclic angular and linear isomeric HQs **105** and **106** reveal λ_{max} ~ 460 and ~600, respectively;[203] whereas 5-6-6-6-5 and 5-6-7-6-5 pentacyclic HQs **70** and **90** serve as NIR dyes with λ_{max} ~ 690–760 and 745–795, respectively.[117] For HQ **6**, the low-lying excited states (in particular, a thermally excited triplet state was detected by EPR, ΔE_{ST} = 0.05 eV) are attributed to its singlet diradical character.[193] For benzoquinone-bridged E,N/E,O bipolar ions **A15** (E = S, **7**; E = Se, **234**) λ_{max} ~ 730.[143,208]

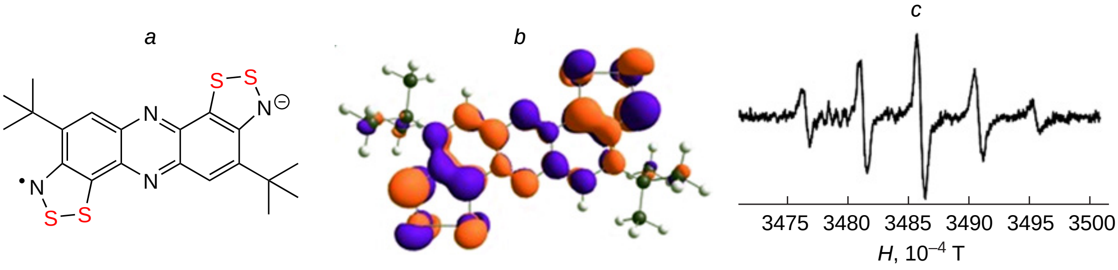


Figure 7. Molecular structure (*a*), the π*-SOMO (*b*), and solution EPR spectrum (*c*) of RA **15**; hfc constant a_N (mT) 0.48 (dithiazole).[117]

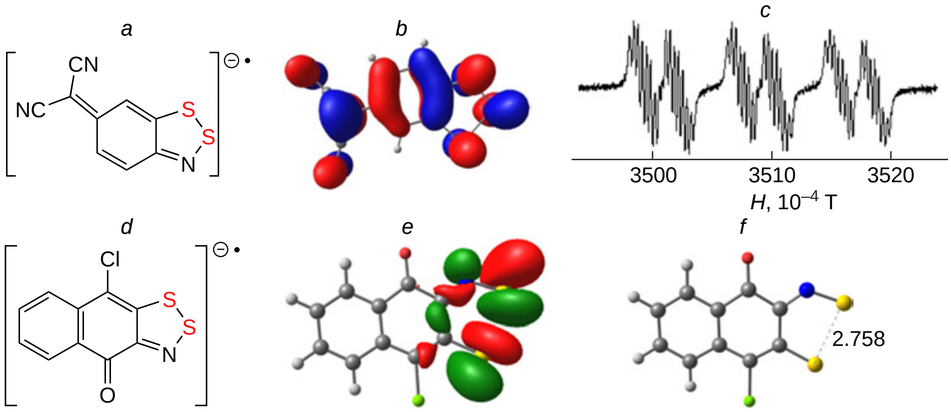
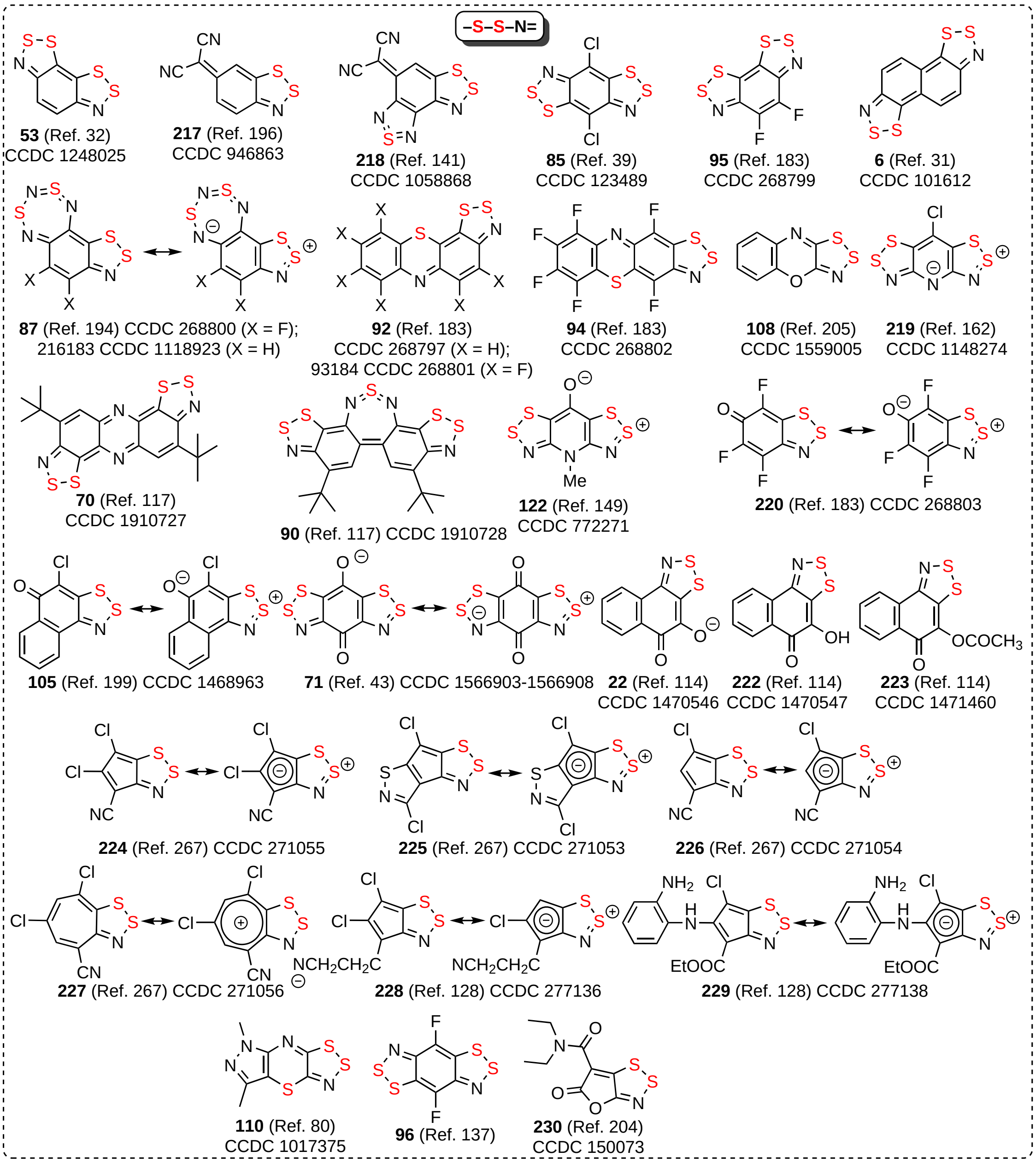
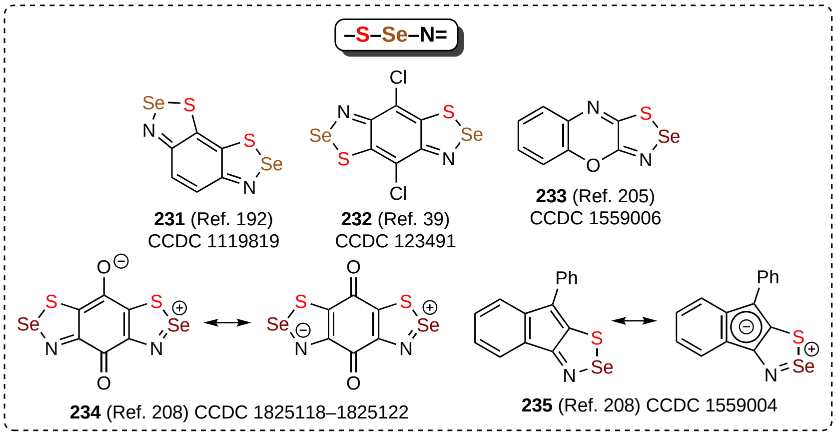


Figure 8. Top: The π*-SOMO and solution EPR spectrum of **114**; hfc constants (mT): a_N ~0.82 (dithiazole) and ~0.04 (CN), a_H ~0.25, 0.10 and 0.01.[196] Bottom: the σ*-SOMO and DFT-optimized structure of **215** with an unusually long S···S distance (Å).[205] Color code: C grey, H light grey, Cl green, N blue, O red, S yellow.





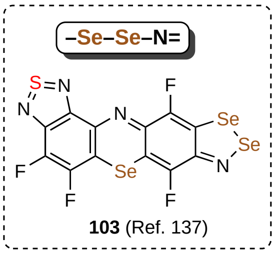
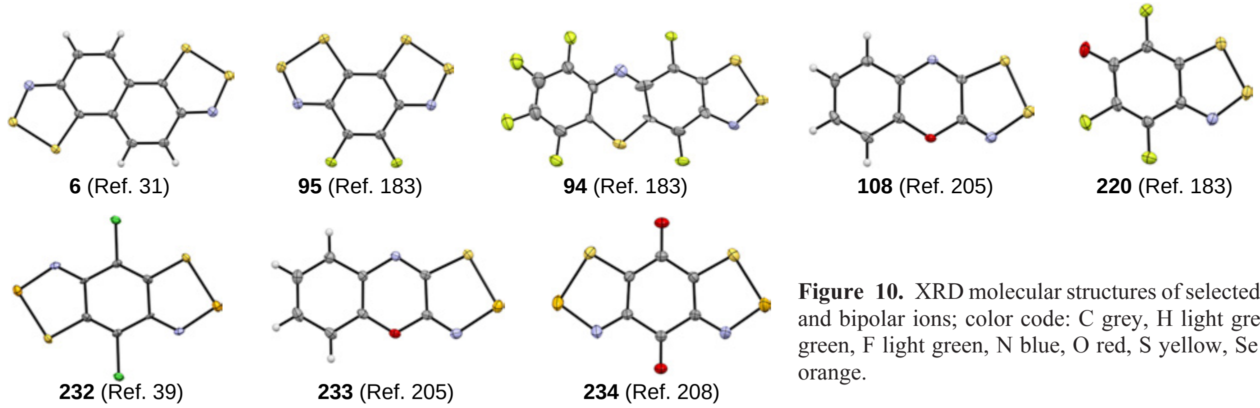


Figure 9. Selected XRD-defined HQs and bipolar ions, and their CCDC deposition numbers. For naphthoxide **221**, cation is $[Li]^+$ in $([Li][\mathbf{221}]\cdot H_2O)_4$.

3.4. Bases

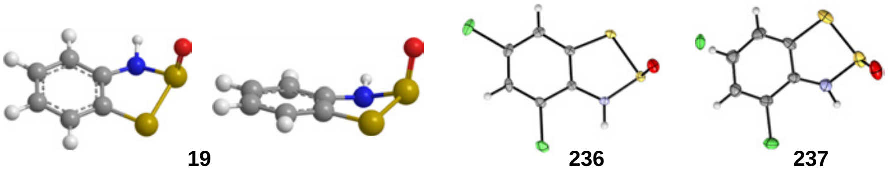
The HBs are structurally defined by XRD only in the form of a dichlorinated compound **236** and 88 : 12 cocrystal **237** of mono- and dichlorinated derivatives;[137] the structures exhibit a shortened N–H···O contact ~2.1 Å (sum of VdW radii, ~2.7 Å),[258] *i.e.* a hydrogen bond, together with planarity of the C–N(–H)–S fragment. According to DFT, this fragment is nonplanar for a free molecule, *i.e.* the N atom is chiral, as well as the neighboring S atom (Figure 11).[137] The presence of two



6 (Ref. 31) **95** (Ref. 183) **94** (Ref. 183) **108** (Ref. 205) **220** (Ref. 183)

232 (Ref. 39) **233** (Ref. 205) **234** (Ref. 208)

Figure 10. XRD molecular structures of selected HQs and bipolar ions; color code: C grey, H light grey, Cl green, F light green, N blue, O red, S yellow, Se light orange.



19 **236** **237**

Figure 11. DFT molecular structure of the archetypal HB **19** and XRD molecular structures of chlorinated HBs **236** and **237** (88 : 12 cocrystal of mono and dichlorinated derivatives).[137] Color code: C grey, H light grey, Cl green, N blue, O red, S olive/yellow.

chiral centres agrees with the observation of diastereomers in solution ^{1}H NMR spectra of HBs.[104]

4. Crystal structure

4.1. Salts

In HSs from the Herz reaction, the anions are typically $[Cl]^-$. Normally, such HSs are poorly soluble in organic solvents due to strong anion-cation electrostatic interactions and do not form single crystals suitable for XRD; acetic and sulfuric acids are more suitable. Metathesis with various low-coordinating anions easily provides HSs soluble in organics. Crystalline HSs [**17**][BF_4], [**23**][BF_4], [**24**][BF_4], [**28**][$GaCl_4$] and [**151**][$GaCl_4$] exhibit centrosymmetric dimers characterized by shortened E2···N3 intermolecular contacts of ~3.24, ~2.87 and ~2.53 Å for E = S, Se and Te, respectively.[33,38,40] The sum of VdW radii of the E and N atoms is ~3.35, ~3.45 and ~3.60 Å for E = S, Se and Te, respectively.[258,268] These shortened contacts are typical of chalcogen-nitrogen compounds, particularly those containing Se and Te, and are indicative of SBIs (*i.e.*, interactions resulting in interatomic contacts that are longer than the sum of the corresponding covalent radii but shorter than the sum of the corresponding VdW radii), namely, ChB driven by σ-holes[269] and enhanced by increasing atomic number/polarizability[270,271] of chalcogen. The holes are regions of low electron density/positive electrostatic potential spatially located on the outer-side extensions of the σ-bonds.[112,269,272–274] In contrast, no shortened intermolecular E···N contacts are observed in [**24**][$GaCl_4$] and [**26**][Cl].[38,103] However, it should be emphasized that for the most studied SBI, *i.e.*, the halogen bond (XB), the interaction distances exceed the sum of the VdW radii up to ~20%.[275]

Owing to ion-ion interactions, most chloride HSs are nonvolatile and exhibit poor solubility in organic solvents, *e.g.*, [**26**][Cl].[103] In contrast, chlorides of isomeric WCs, *e.g.*, **129** and its substituted derivatives, exhibit good solubility, and salt [**129**][Cl] sublimes *in vacuo*.[221] Overall, HCs have a lower propensity to form neutral ion pairs than WCs; however, XRD studies have identified pairs or dimers for chlorides of Bu^t-substituted HCs, which also exhibit high solubility in $CHCl_3$ and CH_2Cl_2.[100,103] Crystals of [**21**]$_2$[Te_4Cl_{18}] exhibit discrete neutral units composed of the anion and two cations and good solubility in $CHCl_3$ and MeCN. In contrast, crystals of poorly soluble [**21**]$_2$[Te_3Cl_{14}] contain an infinite number of double chains of the anions bound by numerous interactions with four chains of the cations.[103]

As mentioned for HCs, the S/Se replacement causes only minor changes in the molecular and electron structures, often manifested in the isomorphism of the S and Se incarnations of HSs. Thus, [HC][$SbCl_6$] (HC = **21**, **145**, **149**, **150**), [HC]$_3$[$SbCl_6$]$_2$[Cl], and [HC][BF_4] (HC = **17**, **26**) are isomorphous; and [HC][$SbCl_6$] (HC = **149**, **150**) form mixed crystals.[38,100,107]

4.2. Radicals and radical ions

In the crystalline state, HRs (see Figure 1) form 0D dimers, 1D stacks, planar 1D ribbons, or 2D layers, whose aggregation results in various 1D-3D architectures. Cofacial dimers typical of chalcogen-nitrogen heterocyclic π-radicals with long E···E intermolecular distances (S···S, ~3.1–3.3 Å) are observed only for the naphthalene/naphthoquinone derivatives **156**/**82** (one of two polymorphs). The dimers of another polymorph of **82** are cofacial only for the heterocyclic moieties; similar dimers are observed for **154**, whereas HR **38**, an isomer of **82**, does not form dimers. HRs **155** and **157** form head-to-tail coplanar dimers. Dimerization by the formation of the C–C σ-bond is known only for **210**. Planar σ-dimers **153**, **204**–**209** are packed into stacks with a strong offset. Stacks of HRs can be equidistant or alternating, perfectly coplanar or not, and with varying degrees of slippage and inclination. Interplanar distances are normally within ~3.3–3.5 Å typical of π-stacking interaction.

The SBIs, manifested by shortened intermolecular contacts, are most typical for the E atoms in position 2. The E2···E2′ contact is often accompanied by the N···E1′ contact forming a cycle composed of N atom and three E atoms. Overall, cyclic supramolecular synthons based on the E···E and E···N contacts are widespread in crystalline HRs and have also been observed in HCs. They form both planar and non-planar ribbons and layers.

Dimorphic resonance-stabilized HRs **A6** and **A7** (E = S, Se) exist in paramagnetic and diamagnetic modifications composed

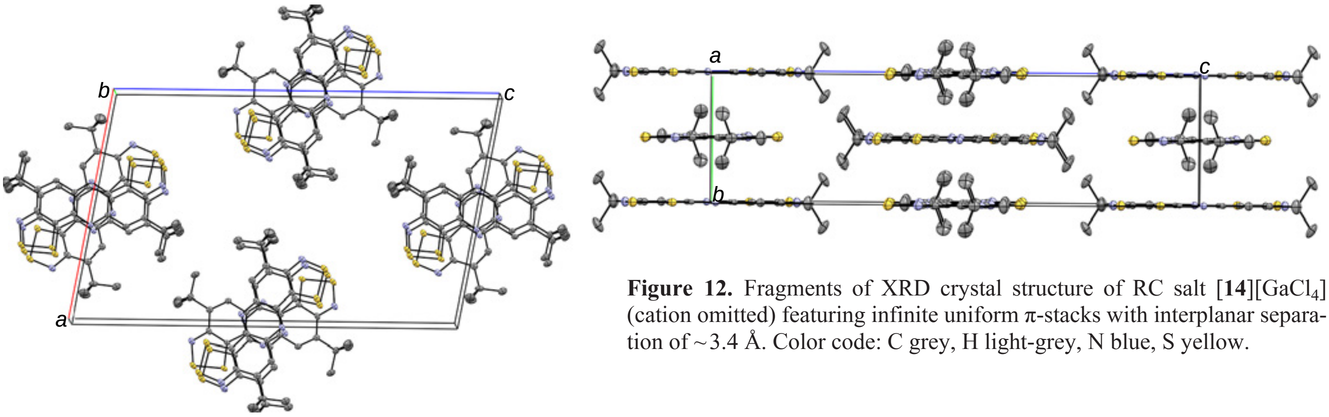
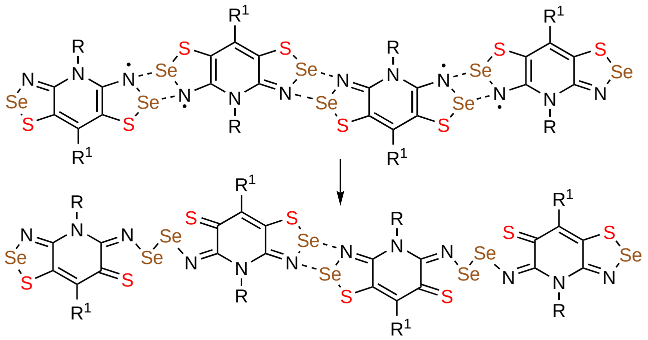


Figure 12. Fragments of XRD crystal structure of RC salt [**14**][$GaCl_4$] (cation omitted) featuring infinite uniform π-stacks with interplanar separation of ~3.4 Å. Color code: C grey, H light-grey, N blue, S yellow.

of individual HRs and their σ-dimers, respectively.[150,176,247] Among paramagnetic modification, the most interesting is the group of isomorphous tetragonal pyridine-bridged HRs. For **175**, **176**, **181**, **182**, **189**, **190**, **194** – **197**, and **201** – **203**, neighboring infinite stacks of HRs are connected by shortened intermolecular E···E and E···N contacts forming columns composed of four parallel stacks. In the stacks, HRs are strongly shifted so that the magnetically interacting SOMOs of the neighbours are nearly orthogonal, allowing ferromagnetic (FM) ordering (see below) in accordance with the Kahn orbital model (KOM), which requires for the FM state a strict orthogonality of magnetically-coupled SOMOs that excludes their spatial overlap; and for the antiferromagnetic (AF) state a non-orthogonality that allows a small overlap.[276,277] The diamagnetic modification is exemplified by the centrosymmetric σ-dimers **153** and **206** – **209** crystallizing isomorphously in the monoclinic space group $P2_1/c$,[147,160,234,236] *e.g.*, the same as for $(SN)_x$.[256] The space group allows approximately coplanar HR ribbons, bridged by four-center $[E\cdots N]_2$ (E = S, Se) SBIs, *i.e.* ChBs, which are suitable for least-motion topochemical conversion of the E–E bonds of HRs into the internal E···E bonds of the dimers (for the formation of σ-dimers by pyridine-bridged HRs, see Scheme 39).[147] The size of the side groups is important for the conversion, *e.g.*, exchanging N–Et of **153** for N–Me of **183** suppresses dimerization of the latter.[160,161] Other space groups observed for related HRs exclude the $[E\cdots N]_2$ SBIs and thus the formation of σ-dimers.[147]

Scheme 39



Structurally-defined radical-ion salts of some HQs, *e.g.*, RC salt [**14**][$GaCl_4$], exhibit π-stacked structures (Figure 12).[117]

4.3. Quinoids and bipolar ions

In the crystals of HQs and related bipolar ions (Figure 9), the most common structural motif is π-stacking with typical interplanar separation of ~3.4–3.6 Å. Bipolar ions display head-to-tail and head-to-head stacking with offset, allowing electrostatic interaction of their unlikely charged parts. Shortened intermolecular E···E and N···E contacts in crystalline HQs and bipolar ions form planar 1D ribbons and 2D layers.

Compound **220** forms non-planar infinite chains with shortened S···O contacts. In crystalline **122**, each molecule is connected by S···O contacts with four others giving rise to 3D structure. Among other oxo compounds, **7** forms 2D layers, whereas **105**, **222**, **223**, and **234** form π-stacks. Nearly planar dimers of **222** are formed by the H···O hydrogen bonds between OH and C=O groups.

Mixed-valence salts formed by RCs **49**, **50**, **63**, **211** with corresponding HQs **6**, **53**, **85**, **231** show stacks with alternating distances and slippage. RC salt [**50**][ClO_4] has no stacks, whereas RC salts [**6**][Cl] and [**14**][$GaCl_4$] form infinite equidistant stacks. Crystals of [**85**][TCNQ] exhibit ...**74** ... **74** ... TCNQ ... TCNQ ... infinite stacks and nearly planar layers, in which each RC and RA contact with four counterions.

4.4. Bases

The crystal packing of HB **236** shows coordination chains with SBIs involving the O, Cl, and H(–N) atoms (Figure 13).[137]

5. Materials science

Herz species are real or potential building blocks of conductive, magnetic and optoelectronic materials. The electrical conductivity of solid HRs is facilitated by a low Coulombic barrier to CT between their π*-SOMOs. For resonance-stabilized HRs, the nature of the spacer and chalcogen atoms, as well as the positions of the atoms, are influential. For some, band-gap closure with formation of the metallic state is observed under external pressure (Refs 31, 32, 34 – 37, 39, 42, 110, 114, 126, 127, 143 – 153, 157 – 162, 192,193, 207, 234, 241 – 252, 265,

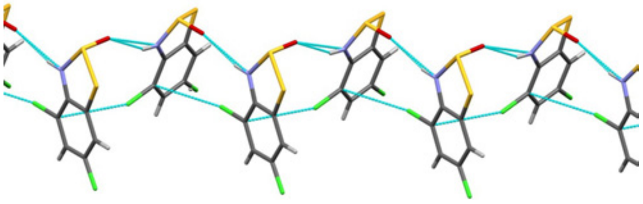


Figure 13. Fragment of crystal packing of HB **236**, dashed lines indicate SBIs. Color code: C grey, H light grey, Cl green, N blue, O red, S yellow.

276, 278–289). From a magnetic point of view, Se and yet unknown Te derivatives are particularly exciting, since the spin density on the heavier atoms with stronger SOC [261,262] allows for increased isotropic and mediated anisotropic exchange effects, magnetic hysteresis and anisotropy, and is involved in singlet fission (SF; *i.e.*, the transformation of a singlet excitation into a singlet spin-correlated triplet pair state, potentially enabling the thermodynamic Shockley–Queisser limit of 33% for the solar cell efficiency to be overcome),[290–292] access to triplet excited states,[293] and triplet-triplete interconvention,[294] which are of interest for materials science. Isotropic and anisotropic FM exchange can also be enhanced indirectly by the incorporation of heavier atoms into nonspin-bearing sites, where they can contribute to multiorbital/multicenter SOC.[288] Such heavier atoms may not only belong to the chalcogen family but also to the halogen family, which is capable of participating in XB,[295,296] *i.e.*, another SBI relevant to σ-hole driven interaction [269]. The latter is especially important; in particular, in crystalline $[Mn(hfac)_2]_3$[**81**]$_2$ (see Scheme 22) the S···O ChBs form Heisenberg spin chains, allowing long-range magnetic ordering.[244] In some cases, external pressure increases the tempetature of bulk magnetic ordering, *i.e.*, the Curie/Nèel temperature (T_C/T_N).

Overall, the S/Se replacement strengthens solid-state SBIs, first of all ChB, towards increasing electrical conductivity and magnetic exchange interactions and magnetic anisotropy.[276,288,289] Many Se-HRs (see Figure 3) are electrical conductors and low-temperature magnetics, *i.e.*, FMs/AFs, in the latter case including also systems spin-canted by Dzyaloshinskii-Moriya mechanism (DMM),[297] *i.e.*, weak FMs; however, heavier-halogen containing HRs (see Figure 3) are less studied. The conductive/magnetic properties of some HRs-based materials are driven not only by external pressure, but also by heat and/or light, making them smart materials.[174,247,280]

Of particular interest are HQs capable of forming stable radical-ion salts, *e.g.*, RC salts [$\mathbf{6}_3$][$GaCl_4$],[157] [**14**][$GaCl_4$],[117] and [**63**][$GaBr_4$],[241] and RA salts,[117,141,196] *e.g.*, [Cat][**114**],[196] promising as both conductors and magnetics. Potentially, even more important is the singlet diradical or quinoidal/Baird (anti)-aromatic character of HQs (in Baird theory, electronically-excited states of ground-state antiaromatics are aromatic;[298–300] in particular, this allows photoswitching of local aromaticity/antiaromaticity [301]). Together with multicenter SOC in heavier-atom derivatives, chromophoric/fluorophoric, redox, and semiconductive properties, these make HQs promising materials for small-molecule optoelectronics [302–305] including unconventional SF materials.[291,306] However, HQs are less studied in these contexts.

The polymorphism, typical of Herz species, obviously affects their conductive, magnetic and optical properties.

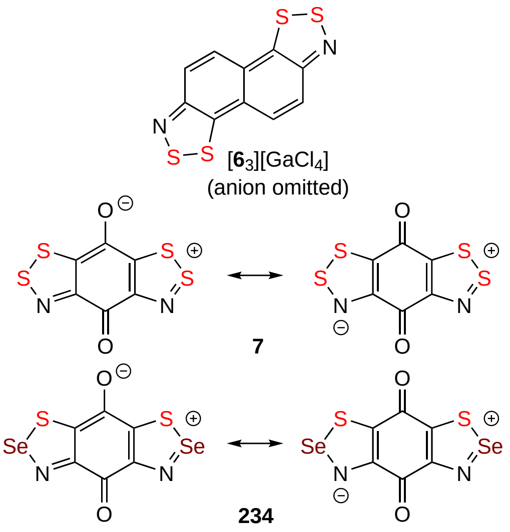
5.1. Conductors

The open- and closed-shell Herz species, *e.g.*, HRs and their dimers, bipolar ions, and mixed-valence salts can be paramagnetic/Mott insulators ($E_a \gg 0$, $\sigma \leqslant 10^{-7}$), semiconductors ($E_a > 0$, $\sigma \geqslant 10^{-6}$) or/and metals ($E_a \sim 0$, $\sigma \geqslant 10^3$; where E_a is the activation energy of the thermal electrical conductivity expressed in eV, and σ is the room-temperature electrical conductivity expressed in S cm^{-1}). Besides the external pressure and SBIs, the electrical conductivity of HRs strongly depends on a complex interplay of many factors, including the nature/molecular positions of chalcogens, the nature/bulkiness of the substituents, the structure and energy of the π*-SOMOs forming the solid-state electron-energy bands. For oxobenzo-bridged HRs relevant to **A4** HCs, the π*-SOMOs can be constructed from group-orbitals of the heterocyles, C=O and other carbocyclic substituents. In this sense, their conductivity is driven by multiorbital effects *via* corresponding electron-energy bands. Exteremely important is the SBIs-related dimensionality of the crystal packing where uniform 1D π-stacks or 2D π-sheets are the most favorable.[143,144,148,155,207,282,283] The **A15** benzoquinone-bridged diradicals/bipolar ions (E = S, **7**; E = Se, **234**) exhibit different crystal packing as $Cmc2_1$ for **7**, and $P2_1/c$ and $R3c$ for two polymorphs of **234**, together with $C2/c$ for **234** · 2 DMI solvate. Normal-pressure (~100 kPa) σ is $\sim 10^{-3}$ for **7** and $R3c$-**234**, $\sim 10^{-5}$ for $P2_1/c$-**234**, and $< 10^{-7}$ for **234** · 2 DMI. High-pressure σ is 1 for $P2_1/c$-**234** (8 GPa), > 10 for **7** (8 GPa), and $\sim 10^2$ for **7** (12 GPa) and $R3c$-**234** (6 GPa), with metallization ($E_a \sim 0$) in the last three cases [143,208] (Table 9).

The σ-dimers **206–209** of pyridine-bridged HRs **169–171** and **174** are small bandgap semiconductors with normal-pressure $\sigma \sim 10^{-6}$; $E_a \sim 0.32$ and 0.36 for **206** and **209**, respectively. At an external pressure of 4–5 GPa, $\sigma \sim 10^{-2}$, 10^{-1}, 1 and 10 for **209**, **207**, **208**, and **206**, respectively. For **206** at ~5–9 GPa, $E_a \sim 0$ indicates metallization. A weakly metallic state arises from intra/intermolecular changes including a collapse of the HOMO–LUMO gap (and hence a near coalescence of the valence and conduction bands, as suggested by solid-state calculations) and increased SBIs, causing band edge broadening and overlap. Near 5 GPa, intramolecular changes include an electronic configuration switch from a hypervalent S–Se–Se–S σ-bond to a π-bonded arrangement *via* buckling of **206** molecules accompanied by a construction in the S–Se–Se–S interatomic distances. The intermolecular changes are a concertina-like compression of the π-stacks. Overall, the σ-dimer → π-HR switch transforms a semiconductor to a metal.[147,234,252]

For the σ-dimer/monomer dimorphic pyridine-bridged **205**/**175**, $\sigma \sim 10^{-7}/10^{-4}$ at 0.5/5 GPa.[150] For the pyridine/pyrazine-bridged **193**/**183**, normal-pressure $\sigma \sim 10^{-3}$; at 8 GPa it increases to 10/1 remaining activated. The benzoxo-bridged solvate **167** · MeCN exhibits $\sigma \sim 10/5–8$ GPa.[147,148,161]

The record normal-pressure σ is ~0.5 for the mixed-valence salt [$\mathbf{6}_3$][$GaCl_4$]; whereas $\sim 10^2$ for E,N/E,O bipolar ions **7** (E = S) and **234** (E = Se) (*i.e.*, **A15**) [143,208] is the record higher-pressure σ (Figure 14). All these values are in the upper part of



[$\mathbf{6}_3$][$GaCl_4$]
(anion omitted)
7
234

Figure 14. Herz conductors with record σ values (see Table 9).

Table 9. Electrical conductivity of solids formed by HRs, σ-dimers, bipolar ions, mixed-valence and RC salts (Refs 31, 32, 34–37, 39, 42, 110, 127, 143–148, 150–152, 155, 157, 159–161, 192, 234, 242, 243, 246, 249, 252, 278, 282, 283).

Herz specie		Conductivity [a,b]	
		σ, S cm^{-1}	E_a, eV
Herz radicals			
–S–S–N•–			
155		10^{-4}	
158		6×10^{-3}	0.16; ≈0 (4 GPa)[b]
160		2×10^{-2}	0.10; ≈0 (3 GPa)[b]
161		4×10^{-3}	0.16
	MeCN solvate	3×10^{-3}	0.11
164		6×10^{-4}	0.21
165		6×10^{-5}	0.24
166		9×10^{-4}	0.27
167	MeCN solvate, polymorphic	4×10^{-2}, 2×10^{-2}; 10 (5–8 GPa)	0.05–0.09
	EtCN solvate	2×10^{-2}	0.14
168		3×10^{-5}	0.20
169		2×10^{-6}	0.41
170		8×10^{-6}	0.41
171		10^{-5}	
172		10^{-5}	
175		10^{-7} (0.5 GPa); 10^{-4} (5 GPa)	
180		5×10^{-6}	0.40
181		3×10^{-6}	0.43
182		4×10^{-7}	0.48
183		10^{-3}; 0.2/5 GPa; 1/8 GPa	0.19; 0.11 (5.5 GPa)
–Se–S–N•–			
186		3×10^{-4}	0.24
188		4×10^{-5}	0.30
189		2×10^{-5}	0.31
–S–Se–N•–			
192		5×10^{-6}; 10^{-3} (4–5 GPa)	
193		2×10^{-3}; 0.5 (5 GPa); 10 (8 GPa)	0.20
194		10^{-4}	0.27
195		5×10^{-5}	
196		2×10^{-5}	
197		10^{-4}	
–Se–Se–N•–			
198		10^{-3}	0.17
Ph-**198**		3×10^{-5}	
199		5×10^{-4}	
Ph-**199**		7×10^{-6}	
200		4×10^{-3}; 2 (5 GPa)	0.17; 0.10 (5 GPa)
201		3×10^{-4}	0.19; ≈ 0 (7 GPa)
202		6×10^{-4}	0.23, ≈0 (9 GPa)[b]
σ-Dimers			
–S–S–			
153		10^{-7}	
–Se–Se–			
205	α-polymorph	10^{-7} (0.5 GPa); 10^{-4} (5 GPa)	0.32; ≈ 0 (5–9 GPa)[b]
	β-polymorph	4×10^{-4} (0.5 GPa); 10^{-4} (5 GPa)	
206		2×10^{-6}; 1 (4 GPa); 10 (5 GPa)	0.32; ≈0 (5 GPa)[b]
207		10^{-6}; 1 (5 GPa)	
208		10^{-6}; 1 (5 GPa)	
209		6×10^{-7}; 10^{-2} (4 GPa)	0.36
Bipolar ions			
–S–S$^+$–N–			
7		10^{-3}; >10 (8 GPa); 10^2 (12 GPa)	0.14; ≈0 (8 GPa)[b]
–S–Se$^+$–N–			
234		10^{-3}; 10^2 (6 GPa) 10^{-5}; 1 (8 GPa)	≈0 (6 GPa)[b] ≈0 (8 GPa)[b]
234·2DMI		$<10^{-7}$	
Radical-cation salts			
[**53**][ClO_4]		10^{-5}	
[**63**][$AlCl_4$]		10^{-3}	
Mixed-valence salts			
–S–S–N=			
[**6**]$_3$[BF_4]$_2$		10^{-2}	
[**6**]$_3$[$GaCl_4$]		0.5	0.18
[**6**]$_3$[$FeCl_4$]		0.4	0.18
[**53**]$_3$[ClO_4]$_2$		10^{-2}	
[**53**]$_3$[FSO_3]$_2$		10^{-2}	
–S–Se–N=			
[**231**]$_3$[ClO_4]$_2$		1	

[a] σ is the electrical conductivity at temperature 295–300 K and normal pressure $\sim 10^2$ kPa; E_a is the thermal activation energy, $E_a \sim 0$ means metallic conductivity/metallization; α and β encode polymorphs. [b] Metallization.

the σ range of conventional semiconductors $\sim 10^{-6}-10^{3}$, and 10^{2} is not far below the Mott–Ioffe-Regel (MIR) limit of metallic electrical conductivity.[305] For HR **160**, a 2D Fermi-liquid (*i.e.*, quantum liquid composed of interacting fermions featuring delocalized states and exhibiting no phase transition) metallic state is observed at 6 GPa.[282] The best thiazyl conductor, polymeric sulfur nitride $(SN)_x$, formally composed of $NS^{\bullet}$ radicals,[50,51] is a genuine metal, exhibiting $\sigma \sim 10^{3}$ ($\sim 10^{5}$ at ~4 K) along the macromolecules and becoming a superconductor at ~0.3 K (0.54 K at 0.9 GPa).[256,292,307,308] The metallic state of $(SN)_x$ is caused by the peculiarities of its crystal packing in the space group $P2_1/c$ leading to the degeneration of the frontier MOs of macromolecules with the formation of half-filled 1D electron-energy band responsible for conductivity. Numerous SBIs (S···S, 3.47–3.70; S···N, 3.26–3.38 Å) transform the Peierls-unstable 1D band into a stable anisotropic 3D one. This situation is unique and the metallic state of $(SN)_x$ is a whim of nature that apparently cannot be used to design other molecular metals; in any case, all known oligomeric analogues of $(SN)_x$ with terminal and/or chain-incorporated arene groups are insulators.[309–312]

The RC salt [**14**][$GaCl_4$], which has not been studied in this context, has uniform π-stacks of the RCs with shortened interplanar spacing in the crystalline state (see Figure 12)[117] and is a potential conductor.

The mixed-valence RC salts $[\mathbf{6}_3]^{2+}[BF_4]_2^-$ and $[\mathbf{6}_3]^{+}[MCl_4]^-$ (M = Ga, Fe) demonstrate nonlinear electrical transport in the charge-ordered insulating state.[31] For M = Ga the room-temperature low-field negative magnetoresistance has been observed,[157] which is rare, *e.g.*, for $(SN)_x$ it has only been detected below ~4 K.[256]

The semiconductive bipolar ion **7**, which exhibits high stability and low solubility in both neutral and charged states associated with strong S-based solid-state SBIs, together with efficient charge delocalzation, is a promising electrode material for lithium-ion batteries. Its Li cells have been successfully cycled at a high rate for 400 cycles with 94% capacity retention, and such Herz species are promising for further design and synthesis of new fast-charging organic electrode materials.[313]

The individual WRs are insulators, but their CT complexes with TCNQ or I_2 are semiconductors with record $\sigma \sim 35$.[224]

5.2. Magnetics

Conductive HRs are are often also bulk FMs/AFs[110,127,148,155,161,250,276,284,287,289,314,315] (Table 10). The most interesting is the **A6** group (see Figure 1, E = S, Se) of isomorphous tetragonal pyridine-bridged/resonance-stabilized HRs **175**, **176**, **181**, **182**, **189**, **190**, **194–197** and **201–203** (see Figure 4), which in the crystalline state exhibit infinite π-stacks connected by shortened E···E and N···E contacts. In the stacks, the magnetically interacting SOMOs of the neighboring HRs are nearly orthogonal, allowing FM ordering according to KOM.[276,277] All FM-coupled HRs **190**, **194**, **197**, and **201–203** contain the Se atom in position 2 and belong to this structural type. Notably, their all-S tetragonal congeners do not exhibit magnetic ordering (*cf.* AF coupled polymorphs of **172** revealing different exchange networks;[245] for **175**, spin crossover[316] between paramagnetic species and their diamagnetic σ-dimers is hysteretic)[150] (some WRs exhibit room-temperature magnetic bistability with hysteric loops of ~10–90 degrees).[224,225,317,318] The only tetragonal 2,1,3-thiaselenazolyl derivative **189** is canted-AF below 14 K. The magnitudes of T_C and coercive fields are higher for all-Se-HRs **201–203** than for their S,Se congeners **190**, **194**, and **197**.

Table 10. Magnetism of solids formed by HRs and RCs.[37,127,145,148,152,159,241,242,245,249,250,278,282,284–286,289]

Herz specie	T,[a] K
	Herz radicals
	–S–S–N•–
158	T_N 4 [b]
160	T_N 13
161	T_N 8 [b]
168	T_N 4.5 [b]
169	$T_N/T_C \sim 5$ [c]
172	$T_N < 2$
180	$T_N < 7$ [b]
	–Se–S–N•–
189	T_N 14 [b]
	–S–Se–N•–
190	T_C 13.6
194	T_C 12.8
197	T_C 14.1
237 [d]	T_N 18
	–Se–Se–N•–
199	T_N 27 [b]
201	T_C 17, 21 (0.9 GPa), 18 (1.6 GPa), 16 (2–4 GPa)
202	T_N 17.5, 24 (2–4 GPa)
203	T_C 10.5, 27.5 (2–4 GPa)
	Radical-cation salts
[**63**][$GaBr_4$] [d]	

[a] Curie or Nèel temperature T_C or T_N, respectively. T_C is the temperature at which paramagnetic substance loses its permanent magnetic properties, and T_N is the temperature above which antiferromagnetic substance becomes paramagnetic. [b] Spin-canted AF. [c] The metamagnet whose magnetic alignment depends on the magnitude of the applied magnetic field H and switches from antiferromagnets to ferromagnet with H = 6–8 kOe. [d] Strongly frustrated AF interactions without bulk magnetic ordering.

DFT, MP2 and CASSCF calculations on π-dimers of HR **169** revealed multicentred bonding similar to that in π-dimers of the phenalenyl radical. The dispersion interaction is the largest attractive term of the bonding,[319,320] and the bonding strength controls the macroscopic magnetic behavior of crystalline **169** (metamagnetism below 5 K)[35,151,278] in such a way that increasing the interdimer distance from ~3.2 to 3.9 Å leads to an AF → FM crossover.[279] Overall, the current awareness of the essential significance of literally omnipresent dispersion interactions in chemistry and materials science should be emphasized.[308]

The σ-dimers **204–209** of pyridine-bridged HRs **169–171**, **174** and **175** are diamagnetic; **205** exhibits a sharp thermal hysteretic (T↑ = 380, T↓ = 375 K) **205** ↔ 2(**175**) interconversion into the paramagnetic state.[147,150] The dimers **204**/**205** dissociating into Curie–Weiss paramagnets **174**/**175** under low-temperature irradiation with visible light at λ = 650 nm can be considered as photomagnetic materials. The photoinduced HR pairs persist up to 150/242 K for HRs **174**/**175**, respectively, before reverting to the dimer states. The Arrhenius activation energies for the HR ↔ σ-dimer interconversion are 8.3 and 19.6 kcal mol^{-1} for 2(**174**) ↔ **204**/2(**175**) ↔ **205**, respectively.

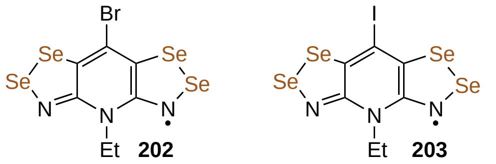


Figure 15. Herz ferromagnets with record T_C values (see Table 10).

DFT and CASSCF calculations suggest that the ground-state interconversion is symmetry-forbidden, and the photochemical one is symmetry-allowed. Variable-temperature high fields/frequencies EPR of **205** below ~380 K has detected ~2% of radical defects, which cannot be assigned to residual **175**.[150,176,247,280]

Overall, the FM ordering of HRs is very sensitive to small changes in molecular and crystal structure caused by chemical modifications of their scaffolds or/and external pressure.[276] The record T_C of 24 and 27.5 are revealed at ~2 GPa by pyridine-bridged all-Se-HRs **202** and **203** (normal-pressure T_C 17.5 and 10.5, respectively; Figure 15), whereas **200** displayed strong AF coupling at lower temperatures.[146,148,243,249,250,287] Among the S/Se pyridine-bridged HRs, **197** showed $T_C \sim 1$ (Ref. 155) (see Figure 15), while **193** showed strong AF coupling.[148] The pyrazine-bridged all-S HR **183** revealed strong AF coupling,[161] while other tested all-S HRs remained paramagnetic.[110] The benzoxo-bridged all-S HR **161** is ordered as a spin-canted AF at $T_N = 8$ at 2 K; for such AFs, field-induced spin-flop transitions to FMs are known.[127] Among other thiazyl magnetics, 4-R-1,2,3,5-dithiadiazolyl (R = 4-NCC$_6$F$_4$), which is spin-canted AF, has $T_N = 36$ K at normal pressure and 70 K at 1.6 GPa.[190,314,315]

The RC salt [**14**][GaCl$_4$] exhibiting uniform π-stacks of the RCs with shortened interplanar spacing (see Figure 9)[117] is potentially magnetic. The RC salt [**63**][GaBr$_4$], having in crystal a kagome-coupled chain structure, exhibits spin frustration.[241]

5.3. Optoelectronics

As mentioned above, some HQs are formal antiaromatics/singlet diradicals featuring low-lying excited states, which may be triplet or singlet;[85,298–301] it is important since most of the functional properties of HQs are π-electronic properties. For small-molecule optoelectronics towards light-emitting diodes, solar cells, and, especially, field-effect transistors, antiaromatics (or, more broadly, π-delocalized scaffolds incorporating $4n$ π-electron subunits)/singlet diradicals are advantageous due to lower first ionization energies and higher first electron affinities (in MO terms, smaller HOMO–LUMO energy gaps and corresponding excitation energies) favorable for charge and energy transport.[99,321–326] Similar compounds are considered an emerging class of organic semiconductors.[66,326–329] With the exception of the HQ-based mixed-valence RC salt [**6**$_3$][GaCl$_4$], the HQs do not belong to the best-conductive Herz species, such as benzoxo-, benzoquinone-, and pyridine-bridged 1,2,3-dichalcogenazole scaffolds. However, HQs are less sensitive to the atmosphere than HRs and exhibit chromophoric/fluorophoric and redox properties. The chromophoric properties of HQs are typically manifested in λ_{max} range of ~460–660,[31,32,39,128,183,194,200] and for **70** and **90** of ~690–760 and 745–795 (*i.e.*, in NIR area), respectively; and **70** has five long-lived and differently colored redox-states.[117] As HQs possess chromophoric/fluorophoric, redox, semiconductive and potentially, multicenter-SOC properties, they are promising materials for small-molecule optoelectronics[302–305] including SF materials.[291,306] More broadly, for heavier-atom HQs any heavy-atom effects[330] typical of chromophores/fluorophores can be expected. However, and in contrast to hetareno/areno-fused 1,2,5-chalcogenadiazoles (chalcogen = S, Se), which have found exciting applications in small-molecule[331,332] and polymer[333] organic optoelectronics, HQs have not yet been studied adequately in this regard. DFT calculations on putative analogues of **A13** (E = S, *cf.* non-fluorinated analogue of **96**) with consequently increasing number of annulated benzene rings bridging terminal 1,2,3-dithiazoles suggest a relationship between the diradical character and the longitudinal second hyperpolarizability (significantly exceeding that of the relevant polyacenes) of these HQs, which can be used in the design of optoelectronic materials.[85] Their naphtho congener **6** (Ref. 31) experimentally exhibits nonlinear optical properties with a large third-order nonlinear susceptibility of 10^{-11} Fr, which can be associated with a number of degenerate electronic states caused by its singlet diradical nature.[193]

6. Conclusion

Contemporary Herz chemistry is a rapidly expanding subfield of future polychalcogen-nitrogen chemistry, encompassing fundamental research and practical applications. Among HRs, resonance-stabilized bridged scaffolds, including σ-dimers, are the most remarkable for materials science, and they and their modifications deserve further attention. Heavier-chalcogen/polyhalogenated Herz species, particularly polyradicals, are the most captivating. A combination of heavier atoms contributing to the overall SOC with multiorbital approach[334] seems especially promising for magnetics. For small-molecule optoelectronics, the antiaromatic HQs typical of Herz chemistry, stabilized by the first-order heteroatom perturbations of π-systems, seem encouraging. Furthermore, even if in the beginning Herz chemistry was focused on HCs/HSs and HBs, and then increasingly on HRs, nowadays, *i.e.*, in its second century, HQs seem the most exciting for fundamental studies and applications. Practically forgotten HBs, still having no Se analogues, are of special interest due to chirality, *e.g.*, as ligands for metal coordination compounds; notably, isomeric 1,3,2-benzodithiazole S-oxides are optically active too.[335] Also, HBs are promising starting materials for HQs, *e.g.*, through thermal transformations. RAs of polyconjugated compounds are potential materials with unusual conductive, magnetic and optical properties,[336] and those of Herz species should be studied intensively. The chemistry and applications of NS$^{\bullet}$ (Refs 50, 51) and its heavier analogues, conventional sources of unpaired electrons for HRs, are also worthy of attention. They are unstable in condensed phase but seemingly can be stabilized as ligands at metal centers, or/and adsorbates in porous frameworks. Notably, NS$^{\bullet}$, in addition to (SN)$_x$, is the archetype of two other (SN)$_n$ (n = 2, 4), binary sulfur nitrides exhibiting non-trivial structure, bonding, and physical and chemical properties.[61,118,337,338] In particular, (SN)$_2$ is proposed for fingerprint and inkjet-trace imaging;[339] while (SN)$_4$ is a strong brisant explosive comparable to pentaerythritol tetranitrate.[340]

While the preparative potential of Herz reactions, particularly hetero-Herz reactions, remains undiminished, the development of novel synthetic approaches and further extension of Herz chemistry to the main-group elements are warranted. The reaction mechanisms remain challenging and demand cutting-edge quantum chemical modeling for a comprehensive understanding.

Finally, an important emerging field beyond the scope of this review is the biological applications of Herz chemistry, which at present mainly involce monocyclic 1,2,3-dithiazoles but show potential for extension to fused derivatives. In any case, and despite synthetic challenges, the 1,2,3-dithiazole scaffold, as well as the 1,3,2-dithiazole one, is promising in the context of various biomedical applications.[46,47,341,342]

7. Terminology, abbreviations and units

The radical-related terms, such as *stable radical*, *persistent radical*, *radical ion*, *radical center*, *etc*, are used as specified by the IUPAC[343] and accepted in common practice.[344]

AC — Appel cation (4,5-dichloro-1,2,3-dithiazolium);
AF — antiferromagnets(ic);
CCDC — Cambridge Crystallographic Data Centre;
ChB — chalcogen bonding;
CT — charge transfer;
DABCO — 1,4-diazabicyclo[2.2.2]octane;
DMI — 1,3-dimetyl-2-imidazolidinone;
DMM — Dzyaloshinskii–Moriya mechanism (of spin canting);
E — chalcogen atom (S, Se, Te);
E_a — activation energy (of thermal electrical conductivity, eV);
$FeCp_2$/$FeCp_2^*$ — ferrocene/decamethylferrocene;
FM — ferromagnet(ic);
HB — Herz base (3*H*-1,2,3-benzodithiazole 2-oxide);
HC — Herz cation (1,2,3-benzodithiazolium);
hfac — hexafluoroacetylacetonate;
hfc — hyperfine coupling;
HQ — Herz quinoid;
HR — Herz radical (1,2,3-benzodithiazolyl);
HS — Herz salt;
KOM — Kahn orbital model;
MIR — Mott–Ioffe–Regel limit (of metallic electrical conductivity);
NCS — N-chlorosuccinimide;
NICS — nucleus independent chemical shift;
NIR — near infrared (area);
OTf — triflate ($[CF_3SO_3]^-$);
RA — radical anion;
RC — radical cation;
SBI — secondary bonding interaction;
SCE — saturated calomel electrode;
SF — singlet fission;
SOC — spin-orbit coupling;
SOMO — single-occupied molecular orbital;
TDAE — tetrakis(dimethylamino)ethylene;
T_C/T_N — Curie/Néel temperature (K);
VdW — van der Waals (radius);
WC — Wolmershäuser cation (1,3,2-benzodithiazolium);
WR — Wolmershäuser radical (1,3,2-benzodithiazolyl);
XB — halogen bonding;
XRD — X-ray diffraction;
a — hfc constant (mT),
δ — NMR chemical shift (ppm);
J — exchange coupling constant (cm^{-1});
λ_{max} — UV-VIS longest wavelength (nm);
q — electrical charge (e);
σ — room-temperature electrical conductivity (S cm^{-1}).
Other abbreviations are standard/common.

Conflicts of interest

There are no conflicts to declare. Alphabetically arranged authors contributed equally.

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